A STUDY OF THE WATER-SOLUBLE
SODIUM PHOSPHATES

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Herman J. Weiser, Jr.

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M.S. University of Cincinnati 1949

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TABLE OF CONTENTS

I. Introduction

The purpose of this research project may be outlined as follows:

A. To study the effect of starting material, temperature and time of heating on the molecular weight or chain length of sodium phosphate glasses having an $Na_2O:P_2O_5$ ratio of about 1:1.

B. To show by direct measurements the polyphosphate nature of the sodium phosphate glasses having an $Na_2O:P_2O_5$ ratio of about 1:1.

C. To study the behavior of the crystalline and glass sodium phosphates on ion exchange resins with the object of separating some of the species.

D. To obtain titration curves with the high frequency titrimeter for the less condensed phosphoric acids.

II. Background and Theory

A. The Crystalline Phosphates

Historically, phosphate chemistry might consider as its starting point the preparation of pure disodium orthophosphate by J. Berzelius (4) in 1816. Although in his analysis of the product he heated it to red heat to dehydrate it and proved its composition to be $2Na_2O.P_2O_5$, it remained for Clark (7) in 1827 to show that the substance obtained by strong heating is chemically different from orthophosphate. In 1833, Graham (14) showed the relationship between ortho-, pyro- and metaphosphates. He also showed that the metaphosphate existed in three forms, a soluble crystalline variety, an insoluble variety, and a soluble glassy variety.

In the period since Graham's work the field of phosphate chemistry has become confused at times. Much of this confusion arose from contradictory systems of nomenclature and inadequacy of analytical methods to establish the degree of polymerization of the phosphates. In recent years a number of reviews (19,31,34,44,45) of the early work have been made which aid in straightening out the confusion.

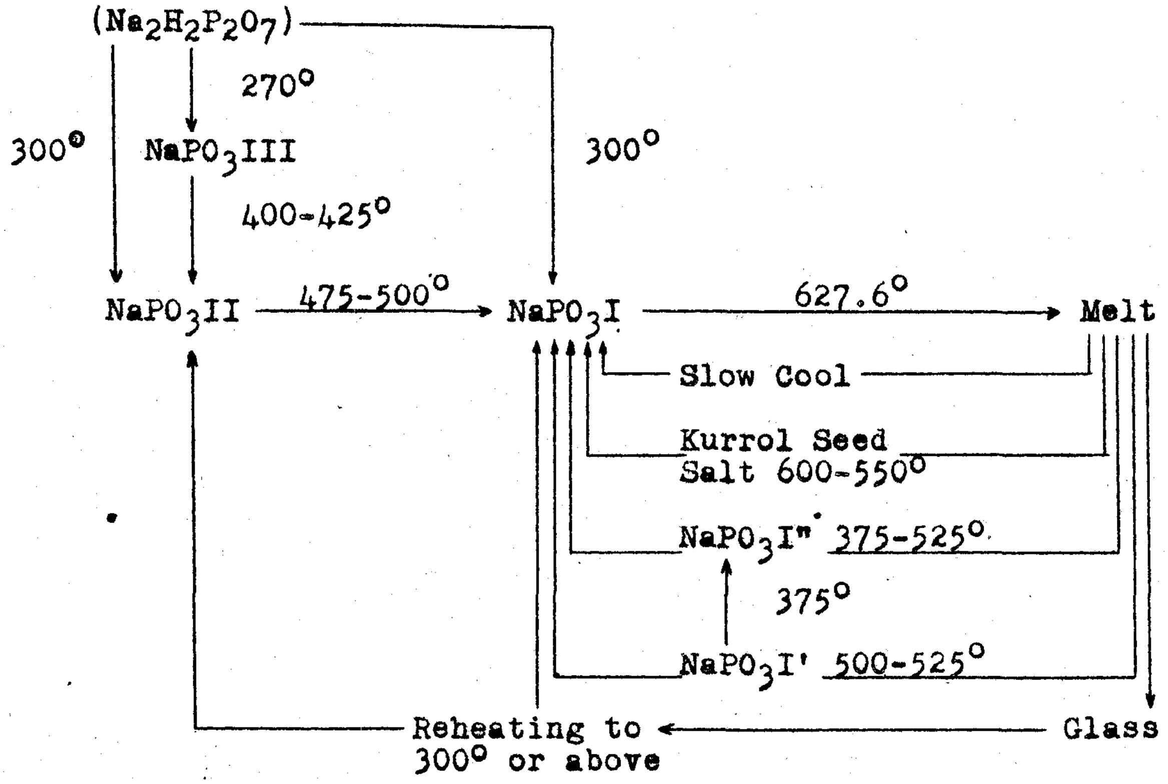
X-ray studies have shown that the types of compounds described in this paper are composed of PO_4 tetrahedra and, for all compounds more condensed than orthophosphate, the phosphorus atoms are linked together by oxygen atoms, i.e., by a P-O-P arrangement.

The compounds to be discussed may be divided into two classes, polyphosphates and metaphosphates. The normal polyphosphates have the general formula $Na_{n+2}P_nO_{3n+1}$. The only crystalline varieties known are orthophosphate Na_3PO_4 (n=1), pyrophosphate $Na_4P_2O_7$ (n=2) and triphosphate $Na_5P_3O_{10}$ (n=3). Although other higher polyphosphates have been reported, it is felt (45) that no chemical individuals have been isolated. The metaphosphates have the general formula $(NaPO_3)_n$. Only two soluble, crystalline metaphosphates have been prepared, trimetaphosphate, $Na_3P_3O_9$ (n=3) and tetrametaphosphate, $Na_4P_4O_{12}$ (n=4). Topley (45) points out that both of these appear to have cyclic structures, the first a six membered ring of alternating phosphorus and oxygen atoms, and the second a similar eight membered ring.

Sodium trimetaphosphate may be prepared by dehydrating NaH_2PO_4 below its fusion temperature (628°C). Liddell (54) has shown by X-ray analysis that sodium trimetaphosphate exists in three different crystalline forms. The preparation of these forms is shown in Figure 1. All three forms of sodium trimetaphosphate, $NaPO_3$I, I', and I", are soluble in water and may be recrystallized from water as the mono- or hexahydrate. $NaPO_3$II and III are crystalline, insoluble metaphosphates whose insolubility indicates a very high degree of polymerization.

Tetrametaphosphate cannot be prepared by heating a sodium orthophosphate (2). It has been prepared (11,6) from

Figure 1. Crystalline Forms of $NaPO_3$.



copper tetrametaphosphate obtained by heating CuO and H_3PO_4 between 350 and 400° in a platinum vessel. The insoluble metal phosphate was treated with Na_2S solution and the sodium salt recrystallized. More recently (45) it has been prepared by hydrating P_4O_{10} with $Na_2CO_3 \cdot 10H_2O$ or a cold suspension of $NaHCO_3$.

Phosphate glasses prepared by fusing phosphates and cooling the melt rapidly enough to prevent crystallization are usually designated by their Na_2O to P_2O_5 ratio. When the ratio is 1:1 the so called "metaphosphate glass" is obtained (also called "hexametaphosphate"). As will be shown later, even this glass seems to have a polyphosphate composition.

A number of analytical methods (3,12,13,18) have been proposed for the analysis of mixtures of the above mentioned ions. For the analysis of mixtures of ortho- and pyrophosphates Farrer and Muir (10) have developed the molybdenum blue method to the point where it can be used to determine small amounts of orthophosphate in large amounts of the other phosphates. Cohn and Kolthoff (8) have developed a polarographic method for determining small amounts of pyrophosphate in 4 to 16 times the amount of orthophosphate. A method which will determine smaller proportions is reported in this paper.

B. Preparation and Properties of Metaphosphate Glasses

The preparation of metaphosphate glass was first reported by Graham (14) in 1834. He heated NaH_2PO_4 to melting and cooled the melt rapidly so that crystallization did not take place. He called the clear, hygroscopic glass obtained, "sodium metaphosphate". It is very soluble and dissolves in water to give a weakly acid solution. The glass has since often been called Graham's salt. Fleitmann (11) in 1849 through the preparation of metallic salts of Graham's "metaphosphate" and analysis of these compounds concluded that the formula $6M_2O \cdot 6P_2O_5$ was the most probable. Fleitmann added that it remained for later investigators to establish this formula definitely. Partridge (31) has pointed out that these later definitive investigations are still lacking.

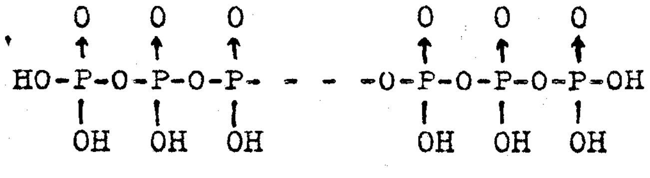
The fact that this formula has not been established is not due to any lack of investigations. Pascal has studied the preparation (32) and structure (33) of Graham's salt and from cryoscopic and ionization data concluded its structure was $Na_2[Na_4(PO_3)_6]$. More recently Mehrota and Dhar (28) have reported the preparation of many soluble complexes by the mechanism:

$$Na_2[Na_4(PO_3)_6] + BaCl_2 \rightarrow Na_2[Na_2Ba(PO_3)_6] + 2NaCl$$

Titration curves have also been used in an attempt to show the structure of Graham's salt. Salih (36,37) prepared the free acid by treating the lead salt with hydrogen sulfide, and titrated it conductometrically. His results indicated that four of the hydrogens were easily dissociated while two were only weakly dissociated. It should be noted that he reported the pH of a 0.1 N solution of the sodium salt to be 9.2. Recent values, and those found by this author, are around 6.2. This indicates that Salih's sample was no doubt contaminated with less highly condensed phosphates. Treadwell and Leutwyler (46) made pH titration curves and concluded that only two of the hydrogens ionize strongly while the other four are weak. More recently Rudy and Schloesser (35) and Van Wazer (47) have made potentiometric studies which indicate that there is one strong acid group associated with each phosphorus atom in the molecule. This allows the phosphate glasses to come under the general rule that in all phosphoric acids there is one strong acid group associated with each phosphorus atom. Rudy and Schloesser, following the proposal of Wilson (52), presented a structure based on a chain of six PO_3 units linked through phosphorus oxygen bonds.

In a series of studies beginning in 1940 Lamm and Malmgren (24,25,26,27) through the use of viscosity, ultracentrifuge and dialysis measurements discovered that samples of Graham's salt had molecular weights of 12,600 and 13,000. They stated that the high molecular weights might be due to micelle formation and not necessarily due to a single molecule. Davies and Monk (9) determined conductivities of sodium metaphosphate glasses down to concentrations of 5×10^{-6} molar. A rapid decrease in equivalent conductance is found between 5×10^{-6} and 5×10^{-3} molar which is attributed to the anion having colloidal dimensions. These authors point out that there is no evidence of micelle dissociation as is found in typical micellar electrolytes.

A 1% solution of a sodium metaphosphate glass is slightly acidic having a pH of about 6.2. An electrometric titration of a solution containing 1 gm. of the glass requires approximately 1.5 ml. of 0.1N NaOH solution between the strong acid end point at pH 4.3 and the weak acid end point at pH 9. Samuelson (38,39) has shown that this weak acid titration is not due to $Na_2H_2P_2O_7$ as suggested by Yost and Russel (53). Samuelson passed a solution of the metaphosphate glass through a cation exchange column to convert it to the acid and then passed the acid through a weak anion exchange column which would absorb ortho- and pyrophosphates but not the glass. The glass came through the column with its weak acid content unchanged and he therefore concluded that the weak acid groups were on the ends of long polyphosphate chains having the structure:



$$\mathrm{HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-\;-\;-\;-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-OH}$$

He therefore proposed that the average molecular weight or average chain length of the glass could be calculated by comparing the equivalents of weak acid with the equivalents of strong acid present in the molecule, assuming there is one weak acid group on each end of the chain. Chain length means the number of HPO_3 or $NaPO_3$ groups present in a molecule. He applied this method to two metaphosphate glasses prepared at 650 and 950°C. and obtained the molecular weights 10,800 and 17,200 respectively.

M. Sibert (40) has compared the titration method of determining molecular weights with the cryoscopic method using the transition point of $Na_2SO_4.10H_2O$ and found the values shown in Table 1. He was using glasses having an $Na_2O:P_2O_5$ ratio greater than one and consequently did not get the high values found by Samuelson.

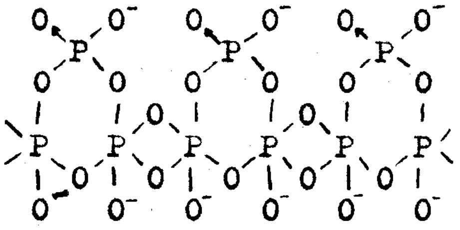
Table 1. Comparison of Transition Point and Titration Molecular Weight Determinations.

Transition Point	Titration
439.2	419
530.0	501
730.6	715
1073.1	1000
1386.5	1327
2082.8	1888

The recent investigations of Van Wazer (49) indicate that the molecular weight found by these determinations is an average of the molecular weights of polymers having greater and lesser molecular weights. A fractional salting out process was used to make a general separation of the polymers in the glass. The glasses were dissolved in water and acetone added until the solution became cloudy. The cloudy mixture was centrifuged and a small amount of viscous oil separated. The average molecular weight of the oil was determined by Samuelson's titration method. Starting with a glass of average chain length 193, he obtained fractions having average chain length values from 550 to 30. When the starting material had a lower average molecular weight, a similar, though not quite as broad, spread of average chain length values were found.

Van Wazer, and Holst (47) have shown that there is one strong acid group for each phosphate atom in a glass chain and state therefore, that since published X-ray analyses of crystalline phosphates have shown that only PO_4 tetrahedra are present, the conclusion may be reached that only unbranched chains and rings composed of interlinked PO_4 tetrahedra exist in solution. They point out that the resonance which stabilizes less condensed forms is appreciably absent in PO_4 groups in which three oxygen atoms are shared. In another paper Van Wazer (48) theorizes that when the $Na_2O:P_2O_5$ ratio is equal to or greater than one only straight chain polyphosphate anions are to be found in solution. He also states that when the glasses are free of water of composition no orthophosphate should be present. But Topley (45) points out that steam is evolved when metaphosphate glasses are crystallized to trimetaphosphate. He suggests that the amount of steam evolved should be measured and compared with the end-group titration and the pH of the original glass. As pointed out above, the pH of a glass solution is about 6.2, and the presence of acid polyphosphates would account for this slightly acid pH. Teichert and co-workers (43) have tried to show that the metaphosphate glasses are merely condensations of trimetaphosphate rings (Figure 2). They base this structure on the need for a meta composition since their titration curve showed no weak acid groups. Their lack of detection of weak acid groups is easily explained by the fact that they tried to titrate 20 ml. of 0.1 N glass solution with 1 N base. This procedure would have little chance of showing the 0.03 milliequivalent of weak acid usually present in this amount of glass. Their structure seems very unlikely from the point of view of the double oxygen bonds between the trimetaphosphate rings.

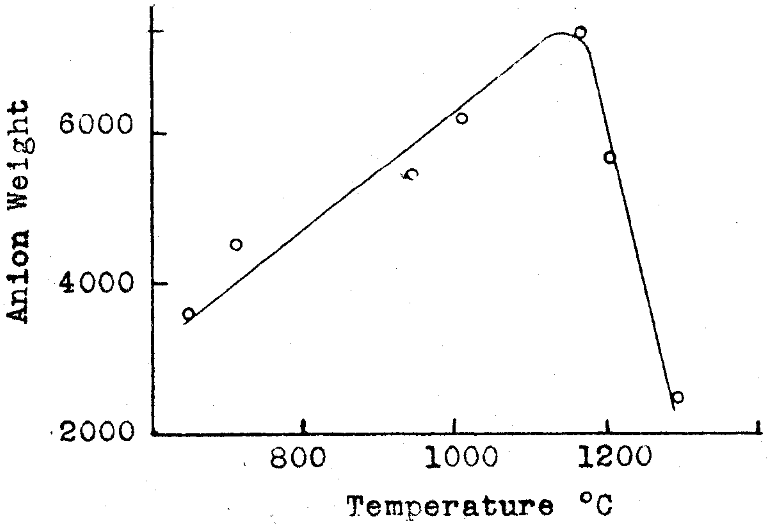
Figure 2. Teichert Proposed Glass Structure



The metaphosphate glasses may be prepared from a number of starting materials, such as NaH_2PO_4, $NaNH_4HPO_4$,

$Na_3P_3O_9$, $Na_4P_4O_{12}$, and others, the only requirement being that the final material has a $Na_2O:P_2O_5$ ratio of one. The material is fused above the melting point (628°C.) for a specified length of time. The final average molecular weight obtained seems to depend upon both the temperature of preparation and the length of time of fusion. Some investigations have been made of the effect of these variables. Karbe and Jander (19) investigated the effect on molecular weight of varying the temperature of preparation. They heated NaH_2PO_4 at 200°C for two hours and followed this by heating at various temperatures for one half hour. The melt was then poured into partially frozen carbon tetrachloride to cool rapidly. The anion weights were calculated from dialysis measurements. Their results are shown in Figure 3. It seems possible that the decrease in anion weight may be due to loss of P_4O_{10} at the higher temperatures.

Figure 3. Variation of Ionic Weight with Preparation Temperature



Samuelson (38) has prepared the glasses at various temperatures by fusing freshly prepared trimetaphosphate for three hours. He determined molecular weight by titration of the weak acid end groups. He found the values shown in Table 2.

Table 2. Effect of Preparation Temperature on Molecular Weight

Temperature of Preparation	Molecular Weight
650°	10,800
750°	12,700
850°	14,300
950°	17,200

Samuelson corrected the dialysis values of Karbe and Jander and concluded that his values were in good agreement with theirs.

Weinberg (50) has prepared the glasses from NaH_2PO_4 and $Na_3P_3O_9$ by fusion at temperatures from 700 to 900°C and at times ranging from 10 minutes to two hours. His values are in general lower than Samuelson's probably due to the shorter time of heating. In fusing trimetaphosphate at the lower temperatures the molecular weight decreased with time probably due to the presence of a large amount of trimetaphosphate being present in the melt heated for only one hour.

A summary of the evidence presented above indicates that the structure of the metaphosphate glasses is that of long chain polymers having a polyphosphate composition. The molecular weight can be controlled to some extent by the temperature and time of preparation. The glasses consist of a mixture of polymers, the average value of which is measured in determining their molecular weights. The possibility of rings being present in the polymers is not ruled out by the evidence now on hand but it seems very likely that Teichert's structure is not correct.

The effect of time as well as temperature of heating on the molecular weight of sodium metaphosphate glasses is reported in this paper. The effect of using different starting materials has been investigated. A method of measuring the combined water and also polyphosphate Na_2O in a sodium metaphosphate glass is presented.

C. Use of Ion Exchange Resins

The use of ion exchange resins has increased very rapidly in recent years. Two books (29,23) have been published which present a very good review of the theory and application of ion exchange resins. Ion exchange resins have been applied to the separation of chemical species which heretofore either could not be separated or yielded only to very long and tedious procedures. Spedding and his co-workers (41,42) and Harris and Tomkins (15) have separated macro quantities of the rare earths from each other in a highly pure form. These resins have also been applied to the separation of amino acids.

The early work in ion exchange resins was carried out using natural and synthetic zeolites but now organic resins, known as organolytes, are becoming very popular. Two types of resins are manufactured, cation and anion exchange resins. The cation resins are generally phenol-formaldehyde polymers containing sulfonic acid or carboxylic acid groups. The cation resin is considered to be a strong or weak resin depending on whether it contains sulfonic or carboxylic acid groups respectively. The weak anion resins contain amino groups and are only effective up to about pH 7. The strong resins contain quaternary ammonium salts and can be used up to pH 10. These resins therefore are insoluble polymers containing ionizable electrolytic reacting groups.

The reaction mechanism in cation resins has been established as an exchange reaction while in the case of anion resins there is still some controversy as to whether the reaction is a true exchange or merely molecular adsorption of the acid molecule. More and more evidence for the true exchange theory is accumulating. Kunin and Myers (21, 22) have shown that the rate determining step in the exchange reaction is the diffusion of the anions into the gel particles. They have shown that as particle size is decreased the rate of reaction increases and further that the rate of stirring has no effect indicating that the reaction is not just at the surface, but inside the resin particle also.

The tendency of an ion to be absorbed by a resin is known as its exchange potential. Kunin and Myers have investigated the effect of valence on exchange potentials and found that the exchange potentials of the anions apparently increase with increase in valence. For a weak anion exchanger, they have found the order for decreasing exchange potential to be: hydroxide > sulfate > chromate > citrate > tartrate > nitrate > arsenate > phosphate > molybdate > acetate = iodide = bromide > chloride > flouride. For a strong anion exchanger the series is the same except that the hydroxyl ion is at the end instead of the beginning, indicating that hydroxyl is the weakest replacing ion.

Ion exchange resins have at present only a few applications in phosphate chemistry. Helrich and Rieman (16) have used cation resins in the determination of phosphate minerals to remove calcium ions. Samuelson, as noted before, has used an anion resin to demonstrate the absence of ortho- and pyrophosphates in metaphosphate glasses. In this case any ortho or pyro ions would be absorbed by the resin, while the glass ions are too large to diffuse into the pores of the resin and are therefore not absorbed.

Since the metaphosphate glasses are apparently made up of polymers of different sizes and since these polymers will have different valences and ionic sizes it should be possible to separate them, under the proper conditions, using anion exchange resins. A separation of ortho- and pyrophosphates is reported in a later section and also the behavior of the less condensed phosphates and metaphosphate glasses on these resins.

D. Use of High Frequency Titrimeter

In 1946 Jensen and Parrack (17) published a description of a high frequency oscillator which could be used as an indicator in analytical work. These authors presented curves of titrations made which were very similar to conductance curves and in some cases showed sharper endpoints. One of the most interesting curves was for orthophosphoric acid vs sodium hydroxide. The third endpoint which cannot be found by potentiometric measurements does show up when this instrument is used.

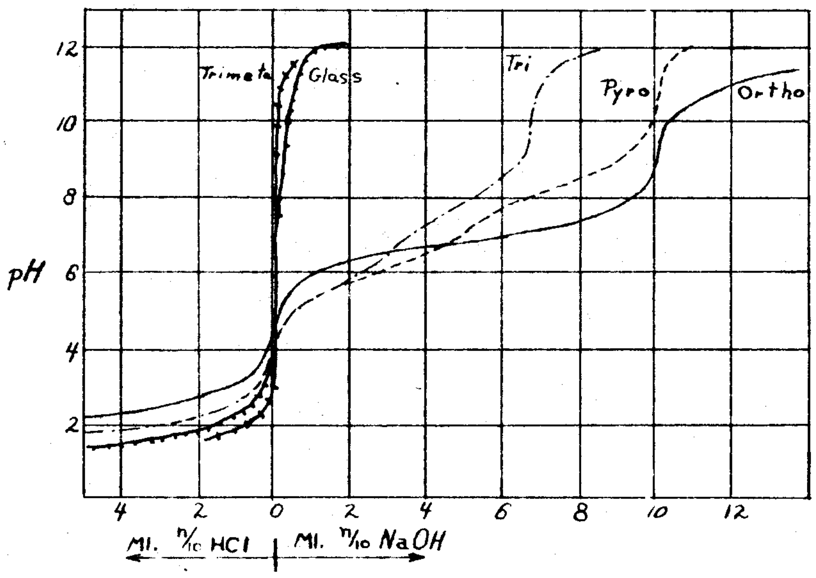
The instrument used by Jensen and Parrack consisted of a tuned-grid, tuned-plate oscillator and a metering circuit. The sample to be titrated is placed in a glass vessel which sits inside the coil of the oscillator. As the content of the solution is changed the inductance of the coil will change and consequently the current through the metering circuit will also change. A full theoretical explanation of what occurs in the high frequency field is not known but it is believed that the effect observed is dependent upon the conductance and dielectric properties of the solution.

The instrument of Jensen and Parrack has been modified by Kremen, Matthews and Borders (20) with a view to increasing its stability. The instrument described by Kremen, Matthews and Borders is very similar to the one used in the present work. Other improved instruments have been described by Anderson, Bettis and Revinson (1), West, Burkhalter and

Broussard (51), and Blaedel, and Malmstadt (5). An interesting developement appears in the paper of Anderson, Bettis and Revinson in the titration of sulfuric acid with sodium hydroxide. Two breaks are found in the curve presented, one after each of the acid groups has been neutralized. Here again the high frequency titrimeter appears to offer advantages over conventional methods in that it can differentiate between the strong acid groups on an acid molecule.

Rudy and Schloesser (35) have presented pH curves for the crystalline phosphates, ortho-, pyro-, tri-, and trimetaphosphates. These curves are shown in Figure 4.

Figure 4. pH Titration Curves for the Crystalline Phosphates



Trimetaphosphate shows a strong acid curve with no weak acid groups. Pyro- and triphosphate each have two weak acid groups which differ only slightly in the titration curve. Orthophosphate shows only one weak acid break, and no break can be found for the third acid group. A metaphosphate glass has also been run, and the curve is very similar to the trimetaphosphate curve except for a small amount of weak acid content.

Curves are presented in a later section for the crystalline phosphates titrated with base using the high frequency analyzer. These curves are compared with those obtained during conductance titrations.

III. Preparation of Materials

The Na_2HPO_4 and NaH_2PO_4 used were twice recrystallized c.p. materials which were partially effloresced in air and then dried in an oven at 110°C. The $NaNH_4HPO_4.4H_2O$ was reagent grade material and was used without further treatment. The pyrophosphate was reagent grade $Na_4P_2O_7.10H_2O$ which was carefully preserved in a well-stoppered bottle. The triphosphate, $Na_5P_3O_{10}.6H_2O$, was commercial material furnished by the Victor Chemical Works and twice recrystallized as the hexahydrate.

Trimetaphosphate and tetrametaphosphate were also provided by the Victor Chemical Works. The procedures developed for their purification as $Na_3P_3O_9.H_2O$ and $Na_4P_4O_{12}.4H_2O$ are described below in detail.

Purification of $Na_3P_3O_9.H_2O$

Sixty grams of commercial trimetaphosphate are dissolved in 250 ml. of water and the insoluble material is separated by filtration. The filtrate is heated to 50°C on a water bath and 250 ml. of 95% ethyl alcohol are added slowly while the solution is well stirred. Precipitation starts when about half of the alcohol has been added. After all of the alcohol has been added the temperature is allowed to fall to 45°C, and the precipitate is separated on a sintered glass funnel. After most of the water has been sucked off the material is air dried. An 85 to 90% yield of the monohydrate is obtained in the form of a fine, crystalline powder.

Purification of $Na_4P_4O_{12} \cdot 4H_2O$.

Sixty grams of commercial sodium tetrametaphosphate ("cyclophos") are dissolved in 450 ml. of water and the insoluble material is separated by filtration. The filtrate is heated to 35°C on a water bath and the solution is well stirred. Alcohol is added rapidly until the solution becomes turbid; then the remainder is added dropwise from a dropping funnel until a total of 400 ml. of 95% alcohol has been added. The needle-like crystals are separated and washed with 100 ml. of 50% alcohol. After air drying, an 85 to 90% yield of the tetrahydrate is obtained.

Purity of Materials and Methods of Analysis

The above mentioned materials have been analyzed for total P_2O_5 and volatile material. The results of these analyses are recorded in Table 3.

The volatile matter analysis was carried out by heating samples of the various compounds for two hours at a temperature of 400°C in a muffle furnace. This loss therefore represents not only hydrate water but also water and ammonia of composition.

As was pointed out in a previous section, Rudy and Schloesser (35) have shown that when orthophosphate is titrated potentiometrically between its strong acid end point at about pH 4.3 and its weak acid end point at about pH 9 one equivalent of acid is titrated for each phosphorus atom. Therefore if any phosphate ion is hydrolyzed to orthophosphate by boiling with HCl, and then titrated between these two end points, the amount of P_2O_5 in the original sample can be calculated. This method is known as the two end point titration method for total P_2O_5 and has been used in determining the percentages of P_2O_5 listed in Table 3. Parallel titrations, using this method, were found to agree within 0.3%.

Table 3. Purity of Materials

Compound	% P2O5		% Volatile	
	Found	Theoretical	Found	Theoretical
NaH_2PO_4	59.4	59.2	15.03	15.02
Na_2HPO_4	49.9	50.0	6.42	6.34
$NaNH_4HPO_4.4H_2O$	35.9	34.0	48.9	51.2
$Na_4P_2O_7.10H_2O$	32.3	31.8	40.2	40.4
$Na_5P_3O_{10}.6H_2O$	45.5	44.7	23.0	22.7
$Na_3P_3O_9.H_2O$	66.2	65.7	5.61	5.56
$Na_4P_4O_{12}.4H_2O$	59.1	59.2	15.03	15.02

The trimeta- and tetrametaphosphates contain only strong acid groups and whem titrated potentiometrically give curves having only one break. Since ortho-, pyro- and triphosphates all have weak acid groups titratable between pH 4.3 and pH 9, their presence in a trimetaphosphate sample would give a curve with two breaks. The titration curve of a trimetaphosphate sample will therefore give a measure of its freedom from polyphosphate impurities. Titration of 0.6 gm. samples of twice recrystallized trimeta- and tetrametaphosphates with 0.1N NaOH detected no weak acid groups. This indicates that the sample is at least 99.8% metaphosphate. It might be pointed out that commercial tetrametaphosphate contains 0.27 equivalents of weak acid per gram and after one recrystallization this is reduced to 0.037 equivalents per gram.

The reagent grade $NaNH_4HPO_4.4H_2O$ had obviously effloresced, but since this was only used in glass preparations, where the amount of hydrate water was not important, and since the $Na_2O:P_2O_5$ ratio was 1:1 as will be shown later, the material was used as received.

IV. Preparation and Composition of Metaphosphate Glasses

Although the glasses described in this section were prepared from materials having a $Na_2O:P_2O_5$ ratio of 1:1, the presence of weak acid groups in the titration curve shows that the glass itself does not have a true meta composition, but has some polyphosphate nature. The titration of these weak acid groups will be the main tool used in characterizing the glasses.

A. Apparatus

All of the preparations at high temperature reported in this section were carried out in a Hoskins muffle furnace equipped with a Leeds and Northrup Micromax Controller and Recorder. The controller cycled continuously within plus or minus four degrees centigrade of the desired temperature. The furnace was equipped with a rheostat which could be adjusted to regulate the range of cycling.

All fusions and high temperature crystallizations were carried out in platinum ware. Preliminary experiments showed that the melts would attack porcelain crucibles very badly, and this contamination caused lowering of the average chain length of the glass. Average chain length values of from 30 to 15 were obtained and these values decreased as the length of the time of heating increased. Nickel crucibles were also tried but an amber colored glass containing nickel was obtained.

B. Average Chain Length Analysis

1. Reagents

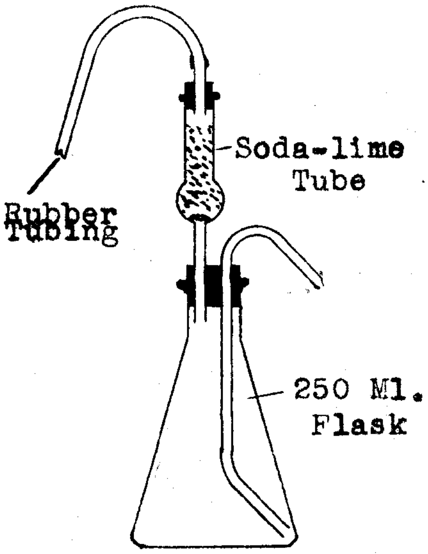
a. Standard 0.1N NaOH.

b. Methyl orange or brom cresol green indicator solution.

c. Approximately 0.5N HCl.

d. Approximately 18N NaOH. (Prepared by mixing 200 gm. NaOH pellets with 200 ml. H_2O. The insoluble material is separated on a sintered glass filter. It is suggested that this solution be stored in a wash bottle like that shown in Figure 5.)

Figure 5. Strong Alkali Dispenser



The NaOH solution can be dispensed by forcing air through the rubber tube into the wash bottle as is done with an ordinary wash bottle. A rubber stopper, bored only three-fourths of the way through, should be placed over the tip of the nozzle so that CO_2 will not be absorbed by any of the solution remaining in the delivery tube.

2. Procedure

An accurately weighed 1 gm. sample of the glass is dissolved in 100 ml. of water in a 100 ml. volumetric flask. A 20 ml. sample is removed, using a pipette, and is hydrolyzed to orthophosphate by boiling for one hour with 5 ml. conc. HCl.

At the same time and using the same pipette a 60 ml. sample is removed. Its pH is adjusted to 3.5 with 0.5 N HCl. The sample is then titrated potentiometrically with 0.1N NaOH. (A Leeds and Northrup Glass Electrode pH Indicator, Model 7662, was used in all of the titrations.) One-tenth milliliter additions are made and the pH read after each addition.

The hydrolyzed sample is made alkaline by addition of saturated NaOH solution using methyl orange or bromcresol green as an indicator. The pH is then brought back to the indicator end point by adding 0.5N HCl dropwise. After cooling, this solution is titrated potentiometrically.

In making the first titration, two weak acid groups are neutralized on each chain while in the second titration one equivalent of base is used for each phosphorus atom. The following equation may therefore be used to calculate the average chain length, $\bar{n}$:

$$\bar{n} = \frac{\text{Ml. base for 20 ml. aliquot after hydrolysis}}{\text{Ml. base for 60 ml. aliquot before hydrolysis}} \times 2 \times 3$$

The total P_2O_5 may be calculated from the milliliters of base required to titrate the hydrolyzed sample, using:

$$\%P_2O_5 = \frac{\text{Ml. base} \times N \times 7.1}{\frac{\text{Wt. of Sample}}{5}}$$

Data for a typical determination are recorded in Table 4.

The method of treating the data to determine the end point was suggested to the author by Dr. O. T. Quimby of the Procter and Gamble Company. The place where the sign changes in the fourth column indicates a point of inflection and thus the general location (within .1 or .2 ml.) of the end point. The more exact value is found by interpolation, i.e., for the first end point shown in Table 4:

$$\text{End Point} = 0.4 \text{ ml.} + \frac{3.3}{3.3 + 4.2} \times 0.1 = 0.44 \text{ ml.}$$

In this example the difference between the end points before hydrolysis is 0.85 ml. and after hydrolysis, 19.22 ml. The average chain length is therefore:

$$\bar{n} = \frac{19.22}{0.85} \times 2 \times 3 = 136$$

It should be emphasized at this point that this average chain length, hereafter known as the Samuelson chain length, assumes that the glass molecules are straight chain polyphosphates containing no orthophosphate nor rings nor branches. Any of these would obscure the meaning of the titration method.

Table 4. pH Data for Chain Length Determination.

Before Hydrolysis

ml.	pH	ΔpH/Δml.	change of ΔpH/Δml.
0.0	4.17		
		1.1	
0.1	4.28		0.5
		1.6	
0.2	4.44		0.9
		2.5	
0.3	4.69		2.5
		5.0	
0.4	5.19		3.3
		8.3	
0.5	6.02		-4.2
		4.1	
0.6	6.43		-1.4
		2.7	
0.7	6.70		-0.8
		1.9	
0.8	6.89		0.0
		1.9	
0.9	7.08		0.2
		2.1	
1.0	7.29		0.5
		2.6	
1.1	7.55		1.3
		3.9	
1.2	7.94		5.3
		9.2	
1.3	8.86		-0.8
		8.4	
1.4	9.70		-4.7
		3.7	
1.5	10.07		-1.4
		2.3	
1.6	10.30		-0.7
		1.6	
1.7	10.46		

After Hydrolysis

ml.	pH	ΔpH/Δml.	change of ΔpH/Δml.
0.0	3.53		
		2.8	
0.2	3.67		0.4
		3.2	
0.4	3.83		1.8
		5.0	
0.6	4.08		1.4
		6.4	
0.8	4.40		-0.8
		5.6	
1.0	4.68		-1.8
		3.8	
1.2	4.87		-0.8
		3.0	
1.4	5.02		-0.8
		2.2	
1.6	5.13		
19.0	7.66		
		2.4	
19.2	7.78		0.2
		2.6	
19.4	7.91		0.8
		3.4	
19.6	8.08		1.6
		5.0	
19.8	8.33		1.6
		6.6	
20.0	8.66		-0.6
		6.0	
20.2	8.96		-1.2
		4.8	
20.4	9.20		-1.2
		3.6	
20.6	9.38		-1.0
		2.6	
20.8	9.51		

C. Effect of Time and Temperature of Glass Preparation.

In all of these preparations the muffle furnace was preheated to the desired temperature before any samples were placed in it. Fifteen gram samples of NaH_2PO_4 were weighed and placed in six platinum crucibles. All of the crucibles were placed in the furnace at the same time. At the intervals noted in Table 5 a crucible was removed and the melt cooled rapidly by pouring it on a cold, stainless steel plate. The glass beads obtained were placed in tightly stoppered bottles. A chain length determination was run on the glasses and the values found are shown in Table 5.

Table 5. Variation of Average Chain Length with Temperature and Time of Heating.

Temperature	Time (hours)					
(°C)	4	8	24	32	48	96
650°	105	108	131	133	138	134
750°	106	122	132	--	153	168
950°	112	150	169	176	169	173

These data are plotted in Figures 6a and 6b. The data follow the general rule that as the temperature and length of time of heating are increased, the average chain length of the glass increases. Figure 6a shows that the average chain length does increase with the time of heating, and, in two

Figure 6a Variation of Chain Length with Time of Heating at Various Temperatures

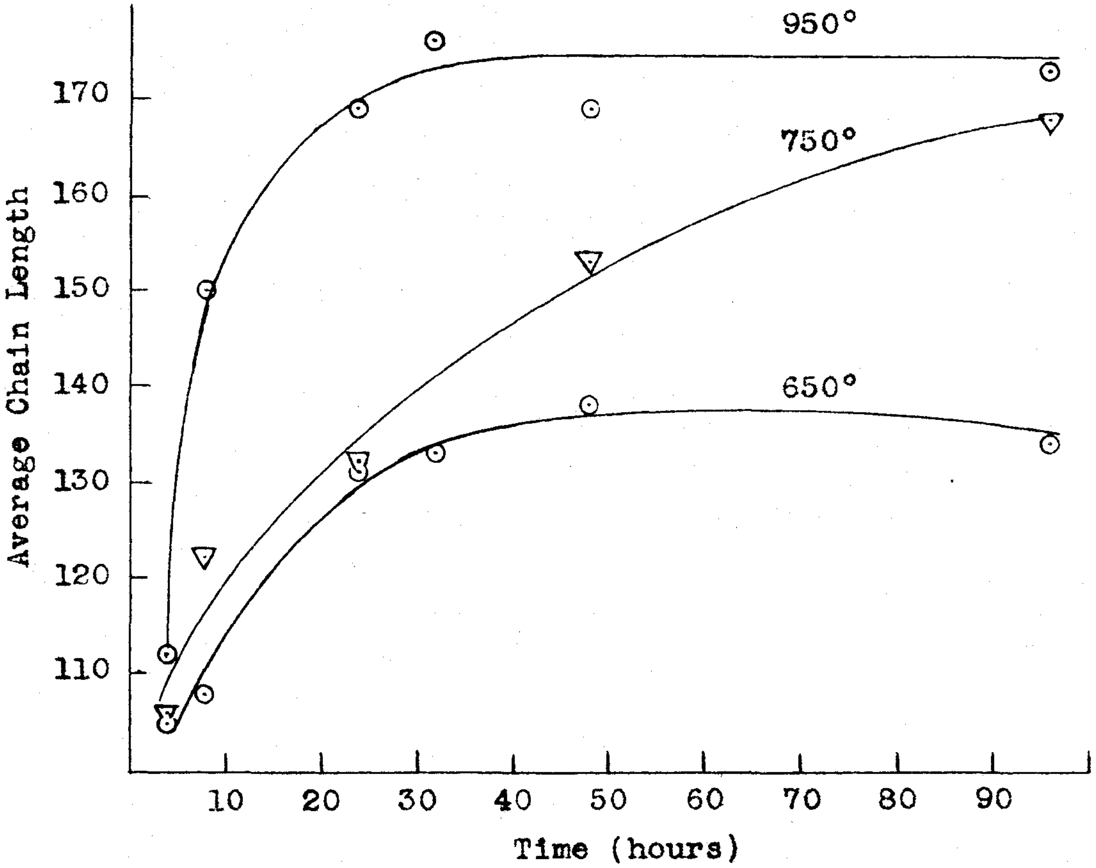
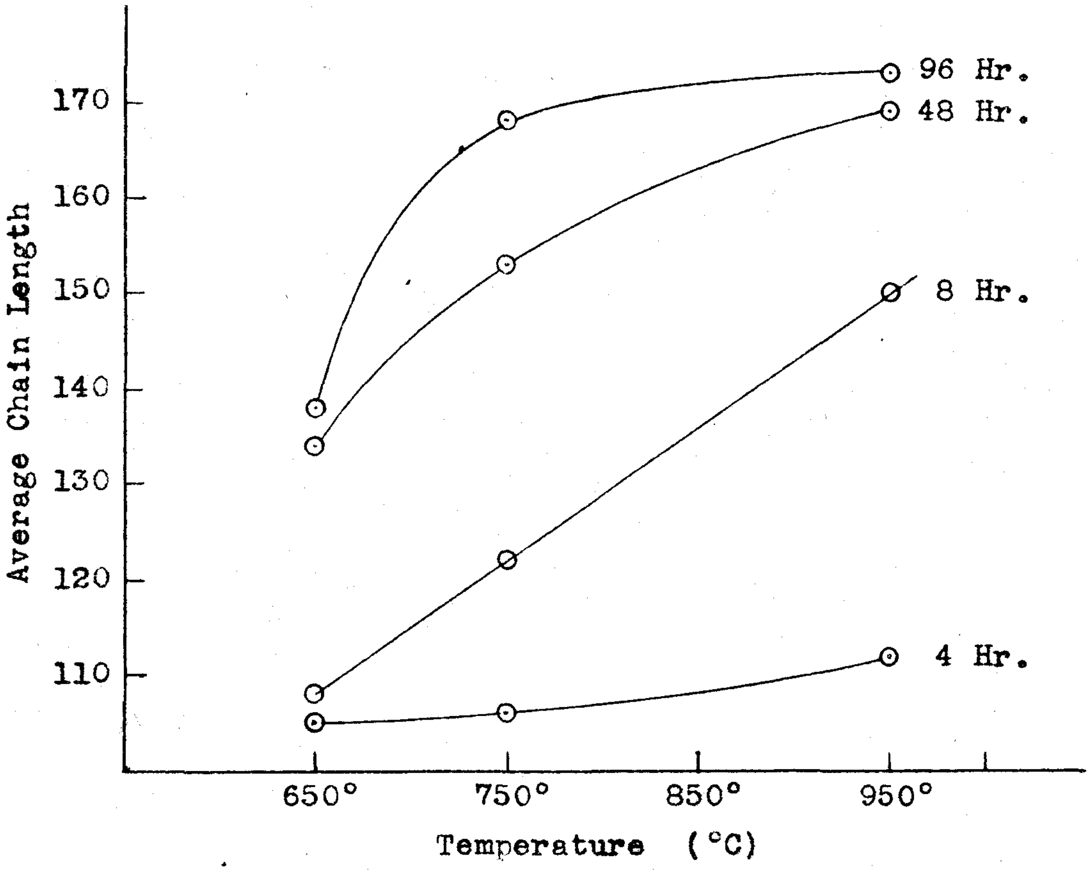


Figure 6b Variation of Chain Length with Temperature of Heating for Various Times



of the cases, the molecular size reaches a steady value. The attainment of the steady state takes place more rapidly at 950°C than at 650°C.

In Figure 6b it can be seen that as the length of time of heating is increased the average chain lengths obtained at the higher temperatures tend to become more alike. The average chain length values for the 650° temperature probably tend to remain low because of the high viscosity of the melt and consequently the slow diffusion of water through the melt. This preparation temperature is only 22°C. above the fusion temperature and in pouring the melts it is easily observed that the viscosity is greater than for melts formed at the higher temperatures. The fusions were not carried to longer periods of time because in several experiments carried out at 144 hours the average chain lengths dropped and the glasses were yellow, probably indicating that some platinum had been dissolved from the crucible.

D. Use of Different Starting Materials.

In Figure 6a it can be seen that although a fairly smooth curve can be drawn through the points, there do seem to be some points which appear erratic. It was therefore decided to see whether a procedure could be set up which would produce the same average chain length even when different starting materials were used.

Four different starting materials were chosen: NaH_2PO_4, $NaNH_4HPO_4 \cdot 4H_2O$, $Na_3P_3O_9 \cdot H_2O$ and $Na_4P_4O_{12} \cdot 4H_2O$. These four differ considerably in their structure, i.e.: single PO_4 tetrahedra with combined water and hydrate water, three membered rings and four membered rings, but all have a 1:1 ratio of P_2O_5 to Na_2O.

The 1:1 ratio of P_2O_5 to Na_2O has been demonstrated by converting these four materials to anhydrous trimetaphosphate (form I). This was accomplished by placing 15 gm. samples of each of the materials in platinum crucibles and first of all fusing them by heating them for one hour at 650°. The furnace temperature was then lowered to 525°C and the melts allowed to crystallize for 17 hours. The crystalline material was removed from the furnace and allowed to cool in a dessicator. After cooling, the material was crushed and placed in well stoppered bottles. An average chain length analysis was run on these trimetas and no weak acid groups were detectable. This indicates that the $Na_2O:P_2O_5$ ratio in these materials is 1:1 and also that no P_2O_5 is lost in this preparation. Any loss of P_2O_5 would leave an excess of Na_2O which would appear as weak acid groups in the analysis of the final materials.

The glasses were prepared in two different ways using the four starting materials. In both cases 15 gm. samples were placed in platinum crucibles and all of the crucibles were placed in the furnace at the same time. All of the melts were poured on a cold stainless steel plate and the time required for cooling and bottling all four was not over twenty minutes. The first two sets of data listed in Table 6 are for samples heated at 650°C for 48 hours. The second set of samples were first converted to trimetaphosphate by the procedure noted and then heated at 650°C for 48 hours.

Table 6. Effect on Average Chain Length of Passing Through Trimeta State in Glass Preparation.

Conditions of Preparation	NaH_2PO_4	$NaNH_4HPO_4 \cdot 4H_2O$	$Na_3P_3O_9 \cdot 1H_2O$	$Na_4P_4O_{12} \cdot 4H_2O$
650°C 48 hr.	112	130	115	128
Same	107	102	117	117
650° 1 hr. 525° 17 hr. 650° 48 hr.	129	139	134	123
Same	124	131	137	139

The data in Table 6 indicate that there is a definite shift in the range of chain length values covered by the duplicate set of samples when the first procedure is used. It seems possible that a change in atmospheric humidity between the days of preparation may have caused this shift. Had the relative humidity increased between the preparations, the water might not have been liberated as rapidly, thus causing more water to be combined with the final glass and lowering the average chain length.

Both of the runs through the trimeta state give higher average chain length values, and both sets cover the same range. Thus taking any of the starting materials through the trimeta state improves the uniformity of the product and gives products of higher average chain length.

In all of the runs made the spread of average chain length values in 15 or 16 units. Since this is constant it seems very likely that it is due to some condition in the process and the most likely one seems to be position in the furnace. Although the furnace chamber is 14 inches deep and heated for over half of this distance, and the crucibles were placed as close together as possible without touching, it seems likely that at this high temperature some slight differences in temperature are present which would account for the spread of average chain length values. Therefore, to get the greatest reproducibility the melt must be placed at the same spot in the furnace.

E. Composition of Metaphosphate Glasses

In this section an attempt is made to obtain information about the composition and structure of the sodium phosphate glasses through titration data. These titrations, similar to those used to determine average chain length, are run on the glass itself and then repeated after the same glass has been crystallized as trimetaphosphate.

1. Materials

The preparative procedures used to obtain the trimetaphosphate and metaphosphate glasses used in this section are outlined in Table 7.

Table 7. Previous History of Analyzed Material.

Starting Material	Preparative Procedure		Analyzed Material
$Na_3P_3O_9 \cdot H_2O$	650°C 525°C	1 hr. 17 hr.	Trimeta
$Na_3P_3O_9 \cdot H_2O$	650°C 525°C 650°C	1 hr. 17 hr. 48 hr.	Glass A
$Na_4P_4O_{12} \cdot 4H_2O$	650°C 525°C 650°C	1 hr. 17 hr. 48 hr.	Glass B
NaH_2PO_4	650°C	48 hr.	Glass C
NaH_2PO_4	750°C	48 hr.	Glass D
NaH_2PO_4	950°C	48 hr.	Glass E

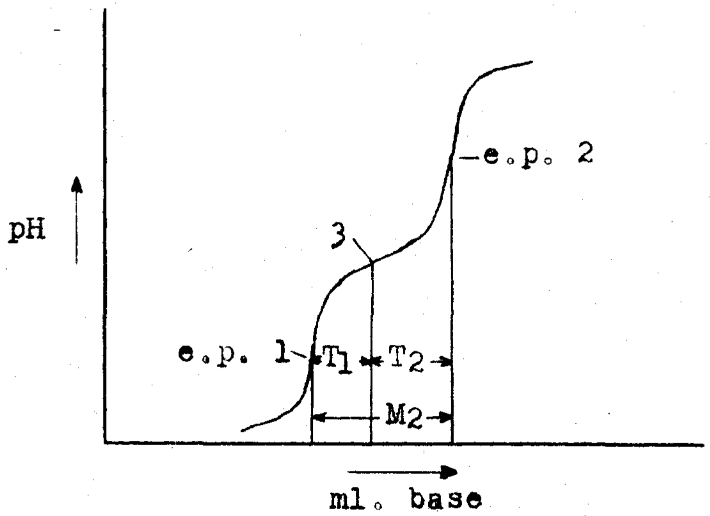
2. Procedure

Five gram samples of a trimetaphosphate and several metaphosphate glasses were carefully weighed in flat bottom platinum dishes. The samples were then placed in the furnace at 650°C. for one hour to melt the glass and form a thin uniform layer. The temperature of the furnace was lowered to 525°C. for 17 hours, during which time sodium trimetaphosphate crystallized and the water in the glass was liberated. The samples were then removed from the furnace and cooled in a dessicator over anhydrous calcium chloride for one hour. The dishes and crystals were reweighed. The samples were then reheated at 525°C. for two hour periods until the loss in weight in each period was only a few tents of a milligram. The percentage of water in the glass was calculated.

The crystalline sodium trimetaphosphate samples obtained were titrated using the same procedure as described on page 26 for the average chain length determination, i.e., 0.6 gm. was titrated for weak acid content and 0.2 gm. was hydrolyzed and titrated for strong acid content. One change in the procedure was made and that was the use of 0.02N NaOH in the weak acid titration instead of 0.1N NaOH. This change increased the sensitivity of the titration considerably.

3. Data and Calculations

In making the weak acid titration of either the glass or the crystallized material the following type of curve is obtained:



E. p. 1 is the strong acid end point and occurs around pH 4.3. E. p. 2 is the weak acid end point and occurs about pH 9. The number of milliliters of base consumed between the end points is represented by M_2 and is equivalent to the number of weak acid groups present in the solution. When a glass or crystallized glass is dissolved in water, the pH of the resulting solution is usually between 6 and 7 and thus falls between the two end points. On the graph above, the pH of such a solution is represented by point 3. The spread between point 3 and e.p. 1, designated as T_1, is a measure of the weak acid groups already neutralized by sodium ions while the spread between point 3 and the end point 2 is a measure of the weak acid groups present as hydrogen ions. If one assumes the linear chain structure of Samuelson for the glass molecule, T_1 is a measure of the

Na_2O present above the 1:1 ratio of $Na_2O:P_2O_5$. Quimby (34) has pointed out that the T_2 spread on the analyzed material will give a measure of the combined water in the molecule. The values found for the various quantities are listed in Table 8 and will be commented upon further a little later.

If it is assumed that all the water lost from the glass during crystallization was present in the glass as weak acid groups, and that all such water was lost, then the number of milliliters of base required to titrate these weak acid groups may be calculated. Under the above assumptions the milliliters of base, T_2(calc.), is given by the following equation:

$$T_2(\text{calc.}) = \frac{(\%\ H_2O)\ (\text{Sample Wt.})}{N\ (.009)\ (100)} \qquad (1)$$

In this equation N is the normality of base used and .009 is the milliequivalent weight of water. Since the sample weight used was 0.6000 gm. and the normality of the base was 0.1031, equation (1) may be simplified to give:

$$T_2(\text{calc.}) = 6.53 \times \%H_2O \qquad (2)$$

In column II of Table 8 are listed the average chain length values found for the glasses by the Samuelson titration method.

✓ It Table 8 the % H_2O found by weight loss on crystallization is listed in column III. By use of equation (2) the $\%H_2O$ is converted to milliliters of base and these values

Table 8. Data on Composition of Metaphosphate Glasses
(Values given in ml. of 0.1N NaOH unless otherwise noted)

I	II	III	IV	V	VI	VII
Analyzed Material	$\bar{n}$	$\%H_2O$	T_2(calc.)	CT_2	IV + V	AT_2
Trimeta	- -		0.13	0.032	0.16	0.054
Glass A	134	0.094	0.61	0.034	0.64	0.75
Glass B	123	0.090	0.59	0.018	0.61	0.74
Glass C	117	0.126	0.82	0.052	0.87	0.85
Glass D	153	0.052	0.34	0.036	0.38	
Glass E	169	0.036	0.24	0.004	0.24	0.48

	VIII	IX	X	XI	XII	
	CT_1	AT_1	$\frac{T_1}{\text{IX-VIII}}$	$\frac{T_1}{AM_2} \times 100$	pH of 1% Solution	
					Analyzed Material	(Re)cryst. Product
Trimeta	0.052	0.052	0.00	0.0%	6.38	6.57
Glass A	0.070	0.10	0.03	3.5	6.22	6.70
Glass B	0.052	0.10	0.048	5.7	6.22	6.86
Glass C	0.062	0.13	0.068	6.9	6.16	6.35
Glass D	0.142					6.92
Glass E	0.210	0.28	0.07	9.2	6.92	7.28

AT_1, AT_2 and AM_2 refer to the analyzed material.

CT_1 and CT_2 refer to the crystallized material.

are listed in column IV. In titrating the crystallized product a T_2 spread is found indicating that some water is still present as combined water and was not removed in the crystallization process. This risidual water is listed in column V. The best value for the amount of water present in the analyzed material is found by adding these two values (columns IV and V). This sum is tabulated in column VI.

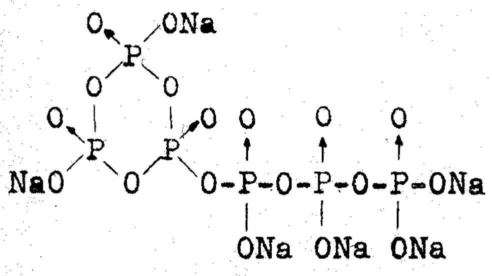
The values of T_2 for the analyzed material are listed in column VII of Table 8. In all cases except two the titration value for combined water (column VII) is greater than the crystallization value (column VI). It appears therefore that some of the combined water is being occluded by the trimetaphosphate crystals during crystallization and are therefore not measured as weight loss. A comparison of the data for Trimeta in columns VI and VII indicates that trimetaphosphate formed in a deep crucible does contain some occluded water, since more water was liberated on crystallization than was present in the Trimeta as weak acid groups.

The data in column VI show that Trimeta does contain a small amount of water. Glasses A and B were both formed by passing through the trimeta state so that they should have contained about the same amount of water before they were fused to form glasses. The resulting glasses contain four times as much water as was present when they were in the trimeta state during their preparation. This indicates that water must have been absorbed from the surrounding atmosphere (air at 650°C.) It appears therefore, that the water content of the glass and therefore the Samuelson average chain length of the glass will depend upon the water content of the air. Glasses C, D, and E were formed at three different temperatures, 650°, 750° and 950°C. respectively. The amount of water present in the glass decreases as the temperature of preparation is increased indicating a more complete dehydration at the higher temperature.

In column VIII of Table 8 are recorded the T_1 titration spreads for the crystallized products. These values measure the amount of Na_2O above the 1:1 ratio of $Na_2O:P_2O_5$ which should be present in a true metaphosphate glass, provided the crystallized product contains only trimetaphosphate and a small proportion of linear molecules. The values in this column for the Glasses C, D, and E, formed at different temperatures, show an increase in neutralized weak acid groups as the temperature of preparation is increased. This indicates that a loss of P_4O_{10} has taken place and as the temperature of preparation is increased the loss of P_4O_{10} increases.

These two facts indicate that the deviation of the composition of a glass from the 1:1 ratio of $Na_2O:P_2O_5$ is due to at least two factors, water content and excess Na_2O. These results present a possible explanation of the maximum found by Karbe and Jander (19) (Figure 3) in their plot of anion weight against preparation temperature. At the lower temperatures the anion weight appears to be dependant on the amount of water lost, but as the temperature is increased the loss of P_4O_{10} tends to counteract the effect of losing water until, above 1200°C., the loss of P_4O_{10} becomes the determining factor and the anion weight decreases.

In column IX of Table 8 are listed the T_1 titration values for the analyzed materials. This is a measure of the excess Na_2O above the meta composition if only linear chains are present in the glass. The fact that the values found for Trimeta in both columns (VIII and IX) are the same indicates that no loss of P_4O_{10} takes place during this recrystallization process and therefore very likely does not take place in the crystallization of the glasses. It is interesting to note that all of the remaining values in column IX are larger than the corresponding values in column VIII. Does this mean that Na_2O is being lost in the crystallization process? This does not seem to be a valid conclusion. The other possibility is that some of the sodium ions which neutralized weak acid groups in the glass are neutralizing strong acid groups in the crystallized product. The presence of rings or branches in the glass molecule would explain this apparent loss of Na_2O. Two structures might explain this change. First a ring with a side chain of the type shown in Structure I.



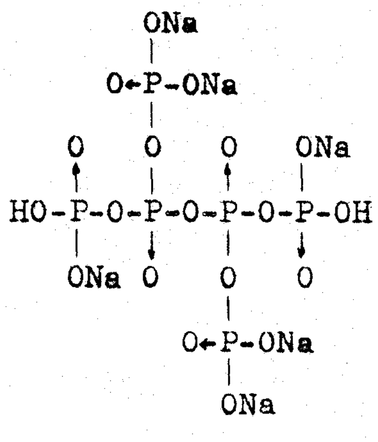
Structure I

It can be seen that at the place where the chain is attached to the ring, a sodium ion has been replaced and this sodium ion will neutralize the weak acid group at the end of the chain. A chain length (Samuelson) determination on this compound will give $\bar{n} = 12$ since there is one weak acid group for six strong acid groups.

$$\bar{n} = \frac{6}{1} \times 2 = 12$$

When this material is crystallized it yields two molecules of sodium trimetaphosphate which contain no weak acid groups so we have apparently lost Na_2O.

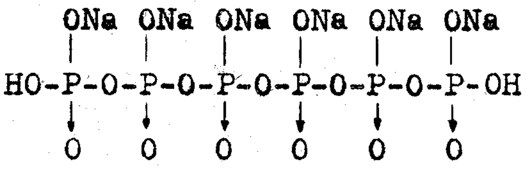
Another possibility is a branched structure like Structure II.



Structure II

In Structure II sodium ions which were originally neutralizing strong acid groups are found neutralizing weak acid groups. A Samuelson chain length determination gives a value of $\bar{n} = 3$ since there are four weak acid groups to six phosphorus atoms. Crystallization of this material yields two molecules of sodium trimetaphosphate and one molecule of water. Again a loss of Na_2O is indicated.

Samuelson based his titration method for determining average chain lengths on a structure of type III.



$$HO-\underset{\underset{O}{\downarrow}}{\overset{\overset{ONa}{|}}{P}}-O-\underset{\underset{O}{\downarrow}}{\overset{\overset{ONa}{|}}{P}}-O-\underset{\underset{O}{\downarrow}}{\overset{\overset{ONa}{|}}{P}}-O-\underset{\underset{O}{\downarrow}}{\overset{\overset{ONa}{|}}{P}}-O-\underset{\underset{O}{\downarrow}}{\overset{\overset{ONa}{|}}{P}}-O-\underset{\underset{O}{\downarrow}}{\overset{\overset{ONa}{|}}{P}}-OH$$

Structure III

The phosphate glasses certainly contain a large amount of Structure III since the apparent loss of Na_2O amounts to only 3.5 to 9% of the total amount of weak acid groups present. The true structure might therefore be a mixture of structures of types I and III, II and III, or I, II and III. It can be seen that each of these combinations will have different effects on the deviation of the Samuelson chain length determination from the actual number of phosphorus atoms in the molecule. The presence of rings at the end of chains will give average chain lengths higher than the true value while the presence of the branching will give lower results than the true value. It will therefore be necessary to run molecular weights by an independant method and then note in which direction the Samuelson method deviates.

The only evidence on hand for making this decision is that given by Sibert (40) and presented on page 9 of this thesis. All of the Samuelson titration values are lower than the values found by depression of the transition point. This would indicate that branching is the predominant type of deviation from a truly linear structure in the glass.

Column XII of Table 8 presents a comparison of the pH of 1% solutions of the analyzed material and the crystallized product. In all cases crystallization has increased the pH of the solution indicating that the water removed from the glass by crystallization is present in the original material as weak acid groups.

F. Conclusions

The following conclusions may be drawn from the data presented in this section:

1. The average Samuelson chain length of the metaphosphate glasses increases as the temperature of preparation and the time of heating are increased.

2. A reasonably reproducible average Samuelson chain length may be produced from any one of a number of starting materials if that material is first converted to trimetaphosphate.

3. The so called metaphosphate glasses appear to be polyphosphates of the general fromula $(NaPO_3)_n(H_2O)_x(Na_2O)_{1-x}$. The relative amounts of water and sodium oxide present depend upon the conditions of preparation, i.e., as the preparation temperature is increased the amount of water decreases and the amount of sodium oxide increases due to a loss of P_4O_{10}.

4. The metaphosphate glasses are not exclusively linear polymers, as assumed by Samuelson, but appear to contain either rings or branches. Present evidence indicates that branching occurs.

5, ~~4~~. Most of the combined water in a glass is ~~in~~ absorbed from the atmosphere and it seems likely therefore that the water content of the air may have some controlling effect on the molecular size obtained.

V. Separation of Phosphate Ions Using Ion Exchange Resins.

A. Resins

All of the resins used were purchased from the Resinous Products Division of the Rohm and Haas Company. The following were used: Amberlite IR-120, a nuclear sulfonic acid cation exchange resin; Amberlite IT-4B, a weakly basic anion exchange resin; and Amberlite IRA-400, a strongly basic anion exchange resin.

B. Apparatus

The ion exchange columns used in this work were 50 ml. volumetric burettes. A plug of glass wool one-quarter to one-half inch in depth was placed in the bottom of the column to support the resin and to prevent the resin particles from plugging the burette tip. A diagram of a typical column us presented in Figure 7a. All of the columns used contained 30 ml. of resin.

Figure 7a Setup for Resin Regeneration

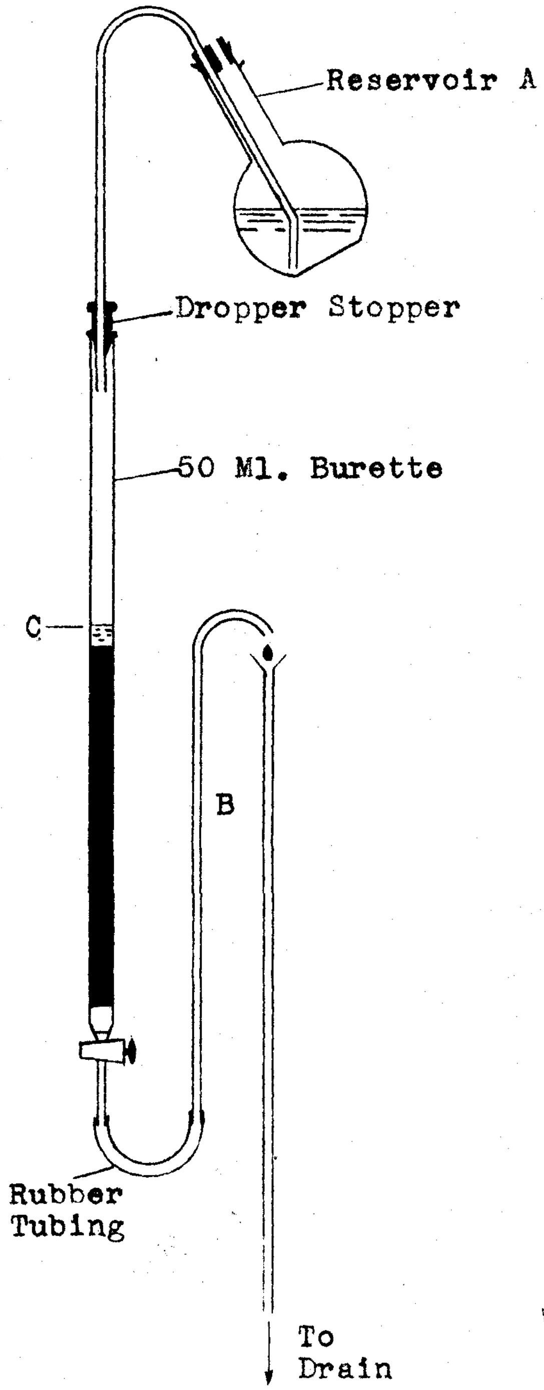
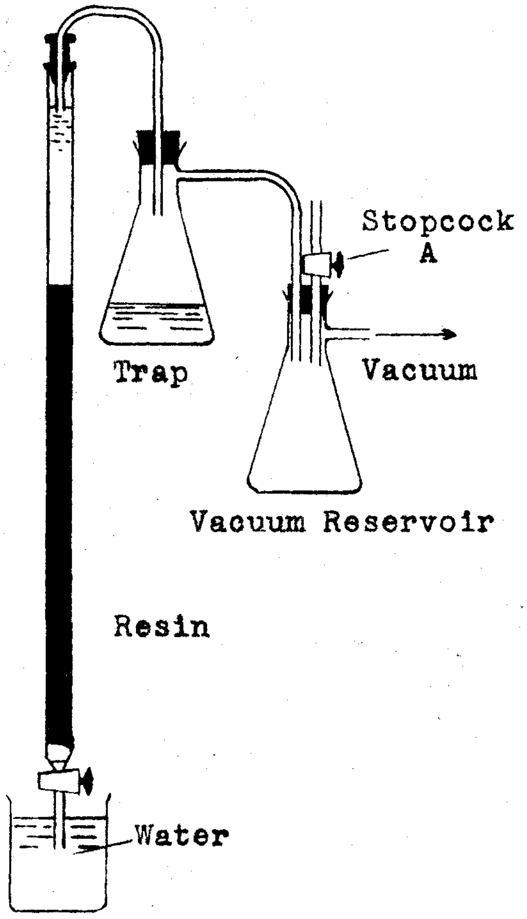


Figure 7b Setup for Backwashing Resin

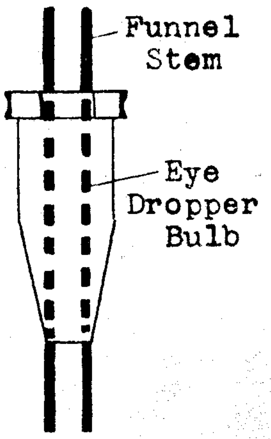


C. General Procedures.

1. Filling Columns with Resin.

The resins were always soaked in water for a day to fully hydrate them before they were placed in the columns. After the glass wool plug was placed in the column, the column was filled with water and a funnel was placed at the top of the column. In attaching this funnel, and in all cases where apparatus or glass tubing was attached to the top of a column, medicine dropper bulbs with the tips cut off were used as stoppers. The conical variety (Figure 8) works best for this job. The tips should be cut off so they fit the tubing which passes through them closely. The resin in the form of a slurry with water is poured into the funnel while water is allowed to flow out at the bottom of the column.

Figure 8. Medicine Dropper Stopper



2. Regeneration of the Resin.

The minimum amounts of reagents necessary to quantitatively regenerate a 30 ml. column of the various resins used are listed in Table 9. The amounts used in the experimental work were always equal to or somewhat in excess of these required amounts. The apparatus was arranged as

Table 9. Regeneration Requirements.

Resin	Regenerant	Ml. Required
IR-120	10% HCl	285
IR-4B	5% NaOH	180
	5% HCl	165
IRA-400	10% NaOH	260
	10% NaCl	230

shown in Figure 7a during regeneration. The regenerant was placed in the reservoir (A) (a 500 ml. florence flask) which is connected by a siphon with the top of the column. The connection at the top of the column must be air tight so that liquid will only enter the column as some is being drawn off at the bottom. The siphon type of arrangement at the bottom of the column (B) prevents the column from going dry by stopping the flow when the liquid in the column reaches level C. This type of arrangement can be made with a minimum amount of glass-blowing ability.

After the regenerant solution had been run through the column, the resin was rinsed with 500 ml. of water. The columns were then backwashed using the set-up pictured in Figure 7b. The amount of vacuum, and consequently the flow rate is controlled by adjusting stopcock A. The rate of flow is adjusted so that the resin fills the column up to the 5 to 7 ml. markings on the burette. Backwashing is continued for 5 to 10 minutes or until the very fine particles have been removed from the resin. The vacuum is then removed and the resin allowed to settle with gentle tapping of the column to aid in uniform packing. This procedure prevents further settling during the final rinsing. The volume of the resin is checked, after the resin has settle, and resin is added or removed to make the volume 30 ml. The column is then rinsed with another 500 ml. of water.

In using these columns to absorb phosphate ions from solution a cylindrical dropping funnel is placed at the top of the column and the effluent is collected in a graduated cylinder. The set-up is shown in Figure 9a. When elutriating the column, the elutrient was fed from a reservoir as shown in Figure 9b. Generally a graduated cylinder is used to receive the effluent, but when NaOH solution is being used a cylindrical dropping funnel is used as a receiver (Figure 9b). It is graduated and equipped with a soda-lime tube.

The flow rate is most readily found by timing the drops falling from the burette tip. It has been found that the flow rate in ml./min. is numerically equal to half the number of drops falling in 6 to 7 seconds, the exact number depending on the individual burette tip. The exact value can readily be found for any particular tip by measuring the volume of a counted number of drops and the time required for them to fall. The value varies only slightly with the content of the solution.

Figure 9a Setup for Absorption

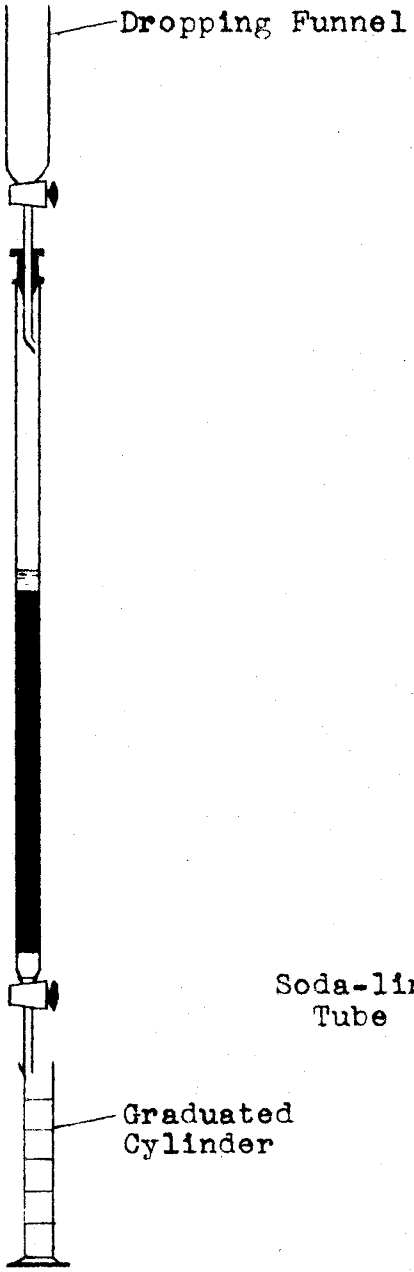
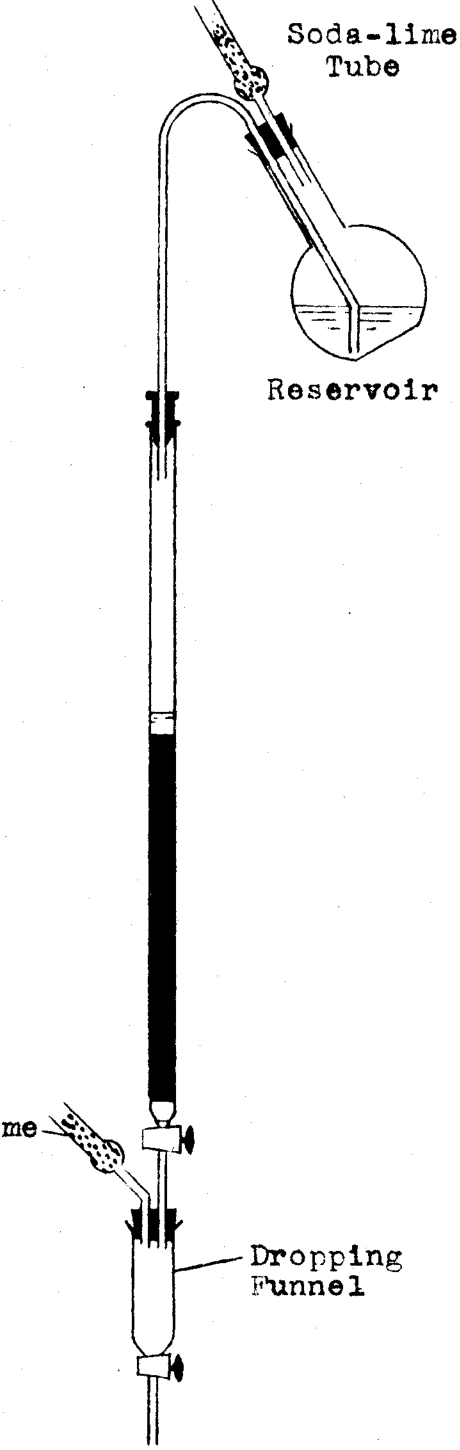


Figure 9b Setup for Alkali Elution

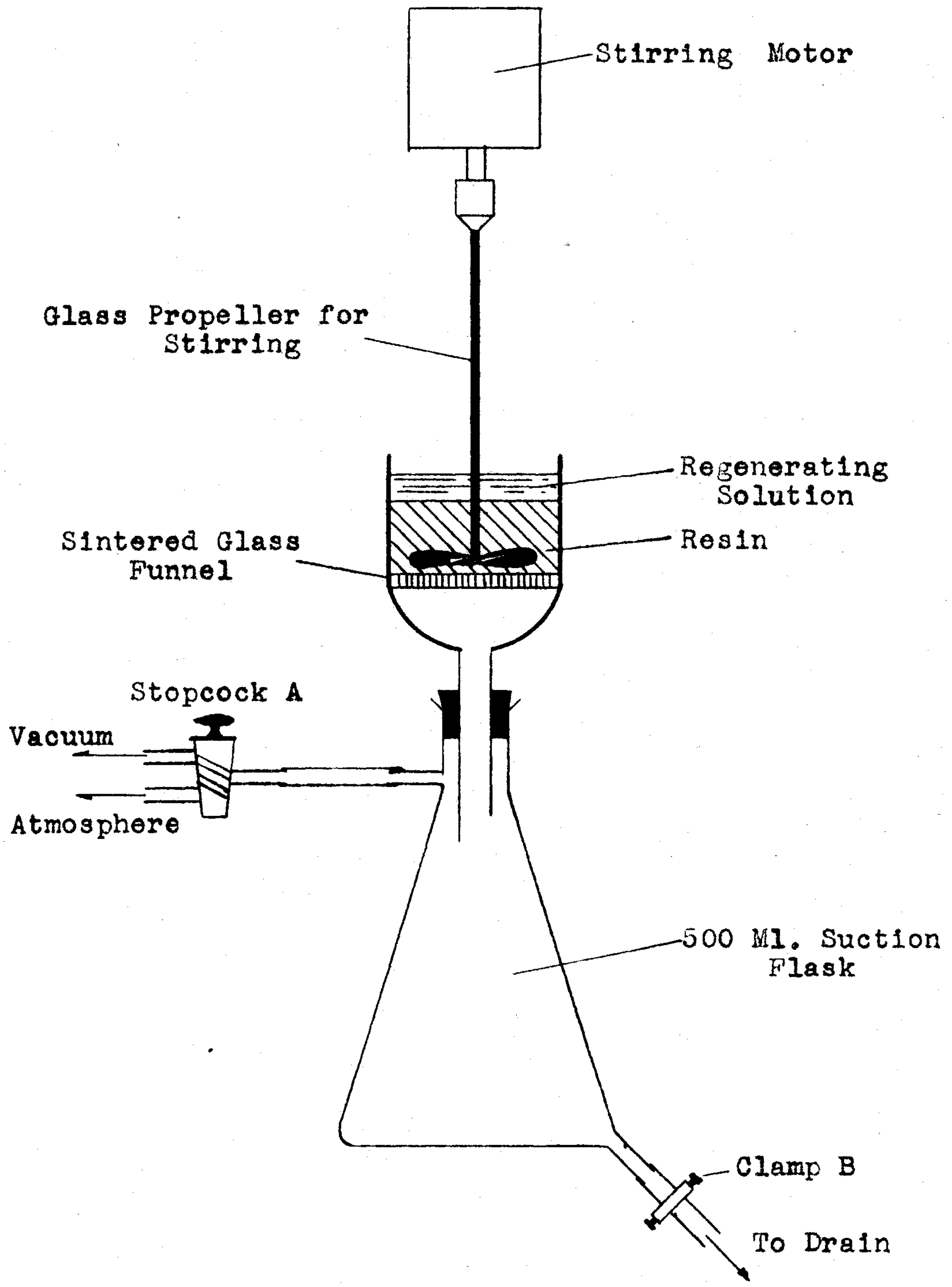


It should be noted that since the strong anion exchange resin absorbs carbon dioxide, it was necessary to remove carbon dioxide from the water used in rinsing or making solutions for this resin. This was readily accomplished by passing the water through a pair of columns, the first containing IR-120 in the acid form and the second IRA-400 in the hydroxyl form. This arrangement completely deionizes the water and in fact furnishes a very good grade of conductivity water. The reservoir A in Figure 7a was equipped with a soda-lime tube when this water was in the reservoir.

At a number of times throughout the work the resins IR-120 and IR-4B were regenerated in a batchwise manner. The apparatus shown in Figure 10 was devised to accomplish this regeneration. The resin was slurried into the sintered glass filter and the water was sucked away from the resin by closing clamp B and opening stopcock A to the vacuum reservoir. The vacuum was then released by opening stopcock A to the atmosphere, and the suction flask was drained by opening clamp B. The sintered glass funnel was then filled with regenerant and the slurry was mechanically stirred for ten minutes, after which the spent regenerant was removed by repeating the process.

This offers several advantages over conventional methods of batch regeneration. Usually the process is carried out in a beaker and the spent regenerant is decanted away from the resin. By use of this apparatus a much better

Figure 10 Apparatus for Batch Regeneration of Resin



removal of spent regenerant is obtained and thus dilution of the fresh regenerant is avoided. The drainage tube at the bottom of the suction flask allows removal of the filtrate without having to dismantle the apparatus. The set-up can therefore be made semi-permanent if a large number of batch regnerations are to be made.

D. Use of Cation Exchanger (IR-120) to Convert Sodium Salts to Acids.

Since the anion exchange resins have a greater capacity for the phosphate ions when they are absorbed from an acid solution, thus causing them to be absorbed in a smaller band at the top of the resin column, it was desired to convert the available sodium salts to their respective phosphoric acids. The strong mineral acids, (HCl, HNO_3, etc.) could not be used because they would introduce another anion which might interfere with or slow down the phosphate absorption or removal from the anion exchange resin. A strong cation exchanger is well adapted for this task because it will absorb sodium ions and replace them with hydrogen ions without adding an interfering anion.

Two methods of exchange were used, columwise and batchwise. In the column operations, 30 ml. of resin were used and after the phosphate solution had been run through the column, 50 ml. of water were run through the column to rinse out all of the phosphate. The exchange was 98% complete, and better than 99% of the phosphate was always recovered.

In carrying out the exchange in a batchwise manner, the resin was measured by volume (30 ml.) in a graduated cylinder containing enough water to cover the resin.

The water was removed by filtration through a sintered glass funnel, and the moist resin was added to the solution of the sodium phosphate. After stirring well for 3 to 5 minutes the resin was removed from the phosphoric acid solution by filtration through sintered glass. The resin was washed twice with just enough water to cover the resin. The washings were combined with the phosphoric acid solution. Exchange by this method is about 95% complete and again better than 99% of the phosphate is recovered.

E. Analyses

All analyses were carried out using potentiometric titrations. The phosphate solutions were hydrolyzed by adding conc.HCl and boiling. Total P_2O_5 analyses were then made by the two end point titration method.

F. Experimental, Data and Results.

1. The Use of the Weak Anion Exchange Resin (IR-4B) in the Hydroxyl Form.

In order to get a general picture of the behavior of the phosphate ions on the weak anion resin, runs were made with ortho-, pyro- and trimetaphosphates. The ortho- and pyro- ions were obtained from their respective acids while trimeta ion was obtained in the acid form by batchwise treatment with IR-120. In each case .011 equivalents of the acid were diluted to 100 ml. and run through the column at 5 ml./min. After rinsing with 50 ml. of water at the same flow rate, 5% NaOH solution was passed through the column at 1.7 ml./min. Twenty milliliter portions of the NaOH solution were collected and analyzed for P_2O_5. An equal volume of starting solution had been analyzed for P_2O_5 so by comparing this latter value with the amount found in each fraction, the percentage recovery in each fraction could be calculated. The values found are recorded in Table 10. The data show that ortho- and pyrophosphates are completely absorbed by the resin, but trimetaphosphate is not. Secondly, in the elution of the ions with 5% NaOH all three ions are removed at nearly the same rate, indicating that the elutrient solution is too strong. When the elutrient concentration is lowered to 0.5% NaOH the same general pattern is followed though the elution is slower. A run was made with orthophosphate

Table 10. Recovery of Phosphates from IR-4B-OH Using 5% NaOH.

Fraction		% Recovery Ortho	 Pyro	 Trimeta
1	100 ml. Phos. Soln.			
	50 ml. H_2O	0.00	0.00	29.6
2	20 ml. 5% NaOH	7.23	7.06	7.04
3	20 ml. 5% NaOH	79.6	75.9	52.0
4	20 ml. 5% NaOH	9.04	10.42	3.38
5	20 ml. 5% NaOH	2.89	2.55	0.99
6	20 ml. 5% NaOH	0.36	--	0.52

using 0.05% NaOH and each of the fractions contained 10 to 11% of the phosphate. Calculations show that the NaOH contained in one fraction is just sufficient to neutralize 9% of the phosphate on the column. This indicates that orthophosphate does not have to be completely neutralized to be removed from the column and that an equivalent exchange is taking place. This gives some support to those who propose that anions are exchanged on these resins and not just molecularly absorbed.

An investigation of the incomplete absorption of trimetaphosphate was made to determine whether the resin had become saturated or whether the exchange had a slow rate. This was done by collecting fractions of the spent phosphate solution as they came off the column. The results are recorded in Table 11. The rate of flow for the absorption part of the

Table 11. Absorption and Desorption of Trimetaphosphate from IR-4B-OH.

Fraction	Content	% Recovery
1	40 ml. Column Water Phos. Soln.	3.47
2	20 ml. Phos. Soln.	4.36
3	20 ml. Phos. Soln.	4.12
4	20 ml. Phos. Soln.	4.43
5	40 ml. Phos. Soln. Rinse H_2O	4.05
6	20 ml. Rinse H_2O	0.00
7	20 ml. 5% NaOH	4.58
8	20 ml. 5% NaOH	66.7
9	20 ml. 5% NaOH	4.98
10	20 Ml. 5% NaOH	1.78
11	20 ml. 5% NaOH	1.06

cycle was decreased to 3 ml./min. and the amount of phosphate retained by the resin increased from 70% to 80%. The amount of phosphate coming through in each of the fractions is nearly the same, indicating that the phosphate break-through is not due to saturation of the resin. The data indicate that the absorption is a slow process, probably because the large cross section of the anion cuts down the speed with which the ion diffuses into the resin particles. The sixth fraction indicates that the resin-phosphate bond is not readily hydrolyzed by water. The NaOH fractions show the usual elution pattern.

When an attempt was made to absorb a short chain length (10.9) glass on this column, only 7.25% of the glass was absorbed. This probably was trimetaphosphate. The experiment does indicate that Samuelson was correct in assuming that glasses would not be absorbed.

Due to the lack of ability to elute the various ions from this resin at different rates and the difficulty in absorbing trimetaphosphate, the weak anion resin (IR-4B) in the hydroxyl form cannot be used for fractionation of the ions.

2. The Use of the Strong Anion Exchange Resin in the Hydroxyl Form.

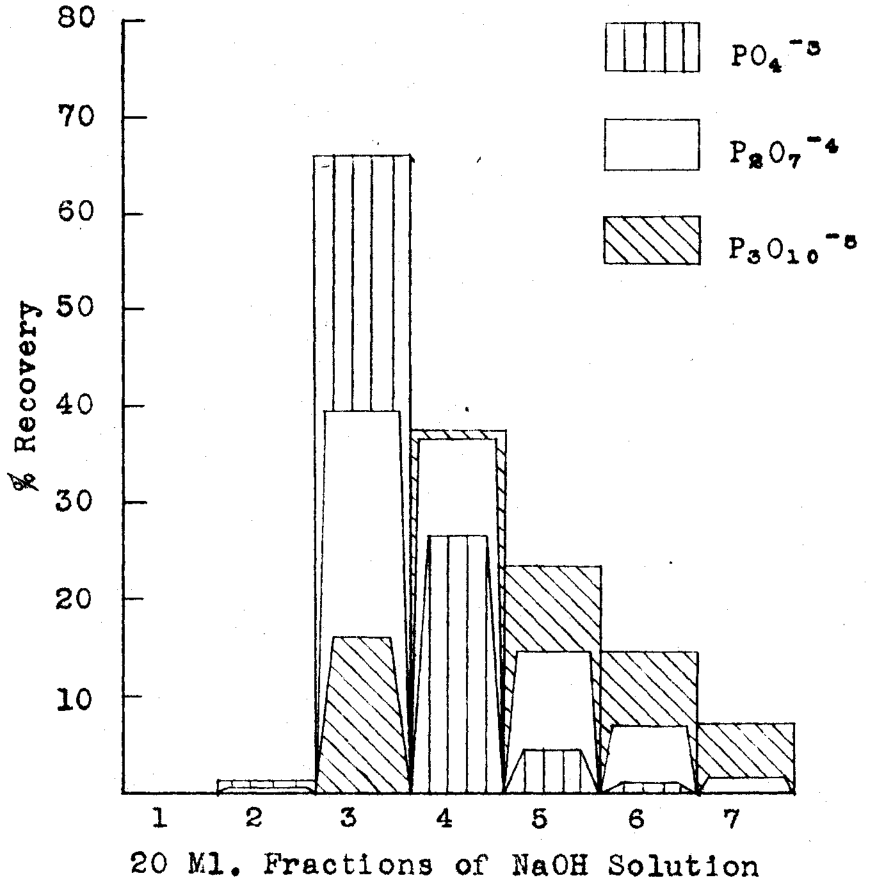
Runs were made under similar conditions to those in the preceding section,ie. 0.011 equivalents of ortho-, pyro-, tri- and trimetaphosphoric acids were run through 30 ml. of the strong anion exchange resin (IRA-400) in the hydroxyl form. Elution was made with 5% NaOH. The phosphates were absorbed at a flow rate of 5 ml./min. and eluted at 17 ml./min. The results of these experiments are recorded in Table 12. The results are presented graphically in Figure 11.

Table 12. Recovery of Phosphate Ions from IRA-400 Using 5% NaOH.

Fraction	Content	% Recovered			
		Ortho.	Pyro	Tri	Trimeta
1	100 ml. Phos. Soln. 50 ml. H_2O	0.00	0.00	0.00	0.00
2	20 ml. 5% NaOH	1.36	0.60	0.00	0.00
3	20 ml. 5% NaOH	67.0	37.3	13.18	2.08
4	20 ml. 5% NaOH	27.1	34.8	30.88	2.41
5	20 ml. 5% NaOH	4.75	13.8	19.35	2.04
6	20 ml. 5% NaOH	1.28	6.47	11.63	1.93
7	NaOH on column 50 ml. H_2O	0.00	1.68	7.27	1.47

The graph shows that there is a tendency for the three

Figure 11 Elution of Phosphate Ions from IRA-400 Using 5% NaOH Solution



ions to be removed at different rates. The ortho comes off rapidly, the pyro a little more slowly and the triphosphate slower than the pyro. The separations are not good in this case because the samples were large, initially occupying one-fifth to one-half of the column.

It is quite clear that, as in the case of the weak resin, trimetaphosphate does not behave similarly to the polyphosphates. It is completely absorbed but it is removed only very slowly. This experiment was repeated and the average chain length of each fraction was determined by titrating the fractions before and after hydrolysis. The results of this run are recorded in Table 13.

Table 13. Percentage Recovery and Average Chain Lengths of Trimetaphosphate Fractions Eluted from IRA-400-OH.

Fraction	Content	% Recovered	Av. Chain Length
1	100 ml. Phos. Soln.		
	50 ml. H_2O	0.00	0.00
2	50 ml. 5% NaOH	4.45	2.02
3	50 ml. 5% NaOH	5.14	3.92
4	50 ml. 5% NaOH	2.25	2.84
5	50 ml. 5% NaOH	3.56	5.13
6	50 ml. 5% NaOH	1.48	3.11
7	50 ml. 5% NaOH	1.65	2.47
8	50 ml. 5% NaOH	2.18	2.58

It has been previously pointed out that trimetaphosphate has no weak acid groups, and therefore its average chain length would apparently be infinite. Orthophosphate has an apparent average chain length of 2, and for pyrophosphate $\bar{n} = 2$, and for triphosphate $\bar{n} = 3$. A mixture of trimetaphosphate with the polyphosphates will give an average chain length higher than in the absence of the trimetaphosphate. For example, if the average chain length of an equi-molar mixture of triphosphate and trimetaphosphate is determined, there will be six strong acid groups to each pair of weak acid end groups, resulting in an apparent average chain length of six. Since the longest polyphosphate which can be obtained from the hydration of trimetaphosphate has $\bar{n} = 3$, an average chain length value greater than 3 for any fraction indicates the presence of trimetaphosphate in that fraction.

The data in Table 13 indicate that some trimetaphosphate is being removed, but most of the material is coming off in the form of the polyphosphate decomposition products.

When a glass of average chain length 10.9 is run in the same manner (Table 14) only 7% of the phosphate can be eluted by 5% NaOH in the same volume as 18.5% of the trimetaphosphate and its decomposition products are removed. Again average chain length determinations show that only decomposition products are being eluted. This indicates that the glasses are held even more tenaciously than trimetaphosphate.

Table 14. Elution of Glass (Ave. Chain Length 10.9) from IRA-400-OH with 5% NaOH.

Fraction	Content	% Recovered	Ave. Chain Length
1	100 ml. Phos. Soln.		
	50 ml. H_2O	0.00	—
2	50 ml. 5% NaOH	0.71	—
3	50 ml. 5% NaOH	1.69	1.96
4	50 ml. 5% NaOH	1.69	2.56
5	50 ml. 5% NaOH	1.61	3.04
6	50 ml. 5% NaOH	1.28	2.62

IRA-400 is a light yellow color and by mixing it with 0.1% phenolphthalein solution before placing it on the column, a resin is obtained which will change color to show the zone in which an anion is abosorbed. The dyed resin is light pink in color after it has been regenerated and rinsed. When a phosphoric acid solution is run through the column the indicator is decolorized where the acid anion is absorbed. This color change is caused by the removal of the hydroxyl ions. The amount of resin required to absorb a certain amount of an anion can thus be readily measured. When NaOH is passed through the column the decolorized band becomes crimson while the remainder of the resin retains its pink color. The crimson color gradually disappears as more NaOH solution is run through the column.

Although this resin does show promise of separating ortho-, pyro- and triphosphate ions, the presence of trimetaphosphate or a phosphate glass will interfere with the separation because of their decomposition products. Trimetaphosphate and the phosphate glasses are retained so tenaciously by the resin that extensive regeneration procedures are required to remove them. This resin therefore does not appear useful for a practical separation.

3. Batchwise Investigations of Weak Anion Exchange Resin.

Since hydroxyl ion is such a strong elutrient on the weak resin, an investigation was made to determine in what other forms the resin might be useful. In looking over the series, three ions appear to be suitable from the point of view of causing no interference in the two end point titration method for P_2O_5. The ions which seem useful are chloride, nitrate and sulfate.

In the first series of experiments the resin was converted to the sulfate form by two regenerations with 10% Na_2SO_4. Various elutrients ($NaCl$, $NaNO_3$ and Na_2SO_4) were used to remove the phosphate. Since sulfate is the hardest ion to displace from the resin, the chloride and nitrate ions should tend to remove phosphate ions before removing the sulfate ions. The following procedure was used in making the runs:

0.2 gm. samples of the anhydrous sodium salts of the various phosphates were weighed and dissolved in 50 ml. H_2O. The pH of the solution was adjusted to 5.0 by batchwise cation exchange of some of the sodium ions for hydrogen ions, followed by removal of the resin by filtration, dilution to 100 ml., and pH adjustment with NaOH solution.

Thirty milliliters of the resin were measured in a graduated cylinder containing enough water to cover the resin. The water was removed by filtration and the moist resin was added to the phosphate solution. The mixture was well stirred for 15 minutes. The solution was then separated from the resin by filtration. The filtrate was hydrolyzed and titrated for P_2O_5. The resin, now containing phosphate, was stirred with 100 ml. of the reagent noted in Table 15 for 15 minutes. After separation of the solution and resin by filtration, the filtrate was again analyzed. The elution process was repeated on the same resin with a fresh portion of elutrient.

Knowing the amount of P_2O_5 in the original solution and having analyzed the filtrates for P_2O_5, the distribution of phosphate between the solution and resin may be calculated. These values are recorded in Table 15 as the ratio of P_2O_5 in solution to P_2O_5 in the resin. The first column in the table is for the absorption of the phosphate and indicates the completeness of absorption. The smaller this number is, the more complete, is the absorption. If the ratios in the elution columns are greater than one the ion tends to come off the resin rather than stay on, while if the ratio is less than one, the phosphate prefers to remain on the resin.

The data show that nitrate ion is a stronger elutrient than chloride ion but that both of these are stronger than sulfate. The sulfate concentration must be increased to 5% in order to get a removal strength equal to 2% $NaNO_3$. In all of these runs the same order of removal of the phosphate ions is indicated, i.e. ortho first, trimeta second, pyro third and triphosphate last. The latter two are not very widely separated, and their separation will no doubt be difficult.

Table 15. Mass Distribution of Phosphate Ions between Solution and Resin.

Ion	Absorption	Elutrient	Elution 1	Elution 2
Ortho	0.154	2% NaCl	1.051	0.729
Pyro	0.018	2% NaCl	0.193	0.091
Pyro	0.020	2% $NaNO_3$	0.493	0.284
Tri	0.00	2% $NaNO_3$	0.433	--
Trimeta	0.022	2% $NaNO_3$	1.20	0.63
Ortho	0.215	2% Na_2SO_4	0.848	0.646
Pyro	0.011	2% Na_2SO_4	0.093	0.076
Tri	0.00	2% Na_2SO_4	0.063	0.027
Ortho	0.193	5% Na_2SO_4	1.45	1.30
Pyro	0.01	5% Na_2SO_4	0.428	--
Pyro	0.019	10% Na_2SO_4	0.986	0.536
Tri	0.012	10% Na_2SO_4	0.833	0.544
Trimeta	0.010	10% Na_2SO_4	0.739	0.370

In order to eliminate the elution of a column in the sulfate form with chloride ion, a series of experiments were carried out on the chloride form of the weak anion exchange resin using sodium chloride solutions as the elutrients. These experiments were carried out using the same procedure previously described and the results are recorded in Table 16.

Table 16. Mass Distribution of Phosphate Ions Between IR-4B-Cl and NaCl Solutions.

Ion	Absorption	Elutrient	Fraction 1	Fraction 2
Ortho	0.39	2% NaCl	2.66	1.30
Trimeta	0.014	2% NaCl	0.697	0.332
Pyro	0.36	2% NaCl	0.401	0.158
Tri	0.010	2% NaCl	0.374	0.118
Trimeta	0.020	5% NaCl	1.50	0.521
Pyro	0.25	5% NaCl	1.08	0.376
Tri	0.015	5% NaCl	1.07	0.305

The data in Table 16 show the same order of elution as previously found. The relative values found indicate that orthophosphate should be easily separable from the other three and that trimetaphosphate may be separable from tri- and pyro-phosphates. The latter two ions are probably very difficult to separate by ion exchange methods.

4. Separation of Ortho- and Pyrophosphates Using IR-4B-Cl.

a. Investigation of Individual Ions.

In order to investigate the column behavior of ortho- and pyrophosphates a number of runs were made with the individual ions using various concentrations of NaCl solutions as elutrients. In these experiments 0.2000 gm. samples of Na_2HPO_4 or $Na_4P_2O_7$ (hydrate actually weighed out) were dissolved in water and treated batchwise with 30 ml. of the cation exchanger to convert them to the respective acids. After removing the exchanger, the phosphoric acid solution was run through the column at 5 ml./min. Fifty milliliters of water were passed through the column at the same rate. The elutrient solution was then passed through the column at 2 ml./min. The results of the runs with orthophosphoric acid are recorded in Table 17 and graphed in Figure 13.

It can readily be seen that one must use 7% NaCl solution to remove the orthophosphate quantitatively in 500 ml. of elutrient. When pyrophosphate is placed on the column and the column is eluted with the above concentrations of NaCl solutions, no phosphate is detectable in the first 600 ml. of elutrient. This indicates that if a mixture of the two ions is absorbed on the column, the orthophosphate can be removed and the pyrophosphate will remain on the column. The pyrophosphate may be quantitatively removed from the column by eluting with

Figure 13 Elution of Orthophosphate from IR-4B with NaCl Solutions of Different Concentrations

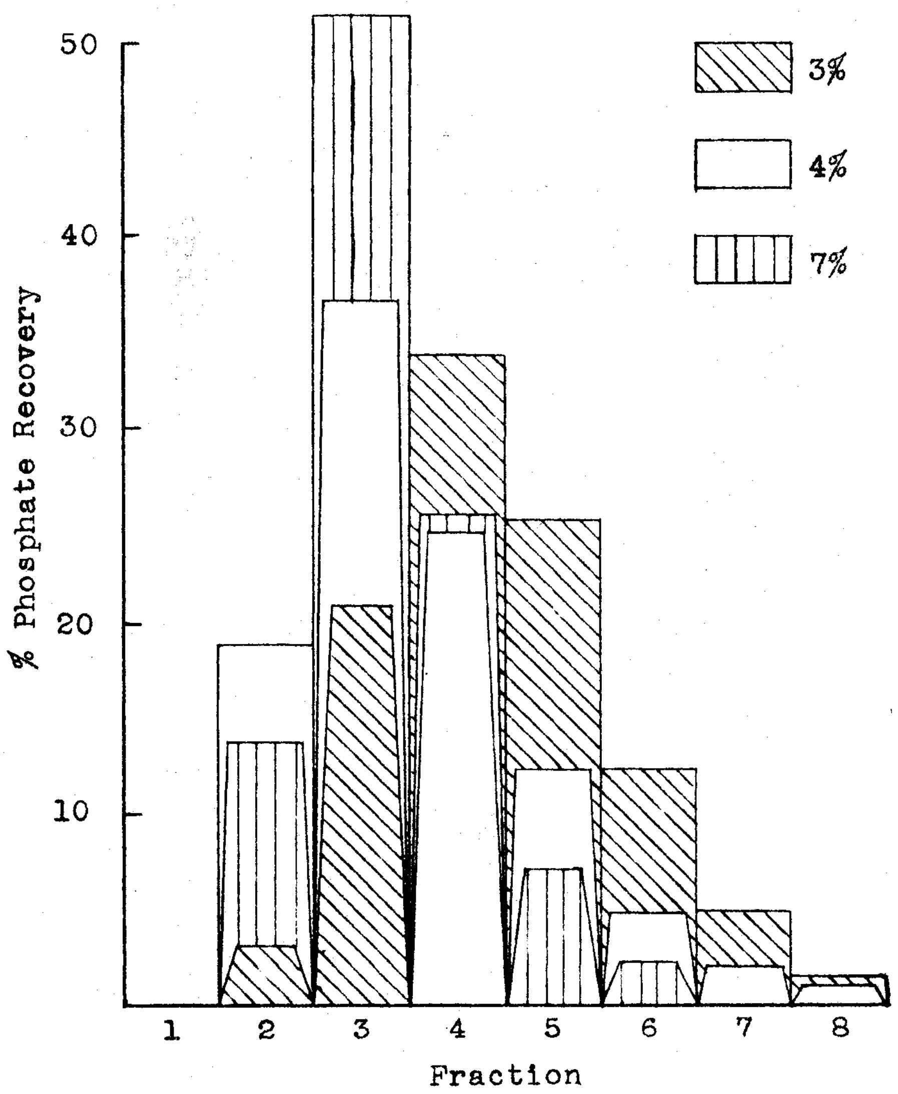


Table 17. Recovery of Orthophosphate from IR-4B-Cl Using NaCl Solutions.

Fraction	Content	Concentration of NaCl Solution		
		3%	4%	7%
1	50 ml. Phos. Soln.			
	50 ml. H_2O	0.00	0.00	0.00
2	100 ml. NaCl Soln.	3.13	18.85	13.72
3	100 ml. NaCl Soln.	20.79	36.70	51.30
4	100 ml. NaCl Soln.	33.79	24.70	25.54
5	100 ml. NaCl Soln.	25.19	12.26	7.18
6	100 ml. NaCl Soln.	12.32	4.78	2.29
7	100 ml. NaCl Soln.	4.82	2.03	0.00
8	100 ml. NaCl Soln.	1.65	1.16	0.00
9	100 ml. NaCl Soln.	--	0.00	--
	Total	101.67	100.48	100.03

400 ml. of 5% HCl at 2 ml./min. Hydration of the pyrophosphate will take place in this strongly acid solution but this is not important if one only wishes to know how much pyrophosphate was present in the original mixture. On the basis of the information presented above, the following procedure has been set up for the determination of ortho- and pyrophosphates in a mixture of the ions.

b. Determination of Ortho- Pyrophosphate Mixtures.

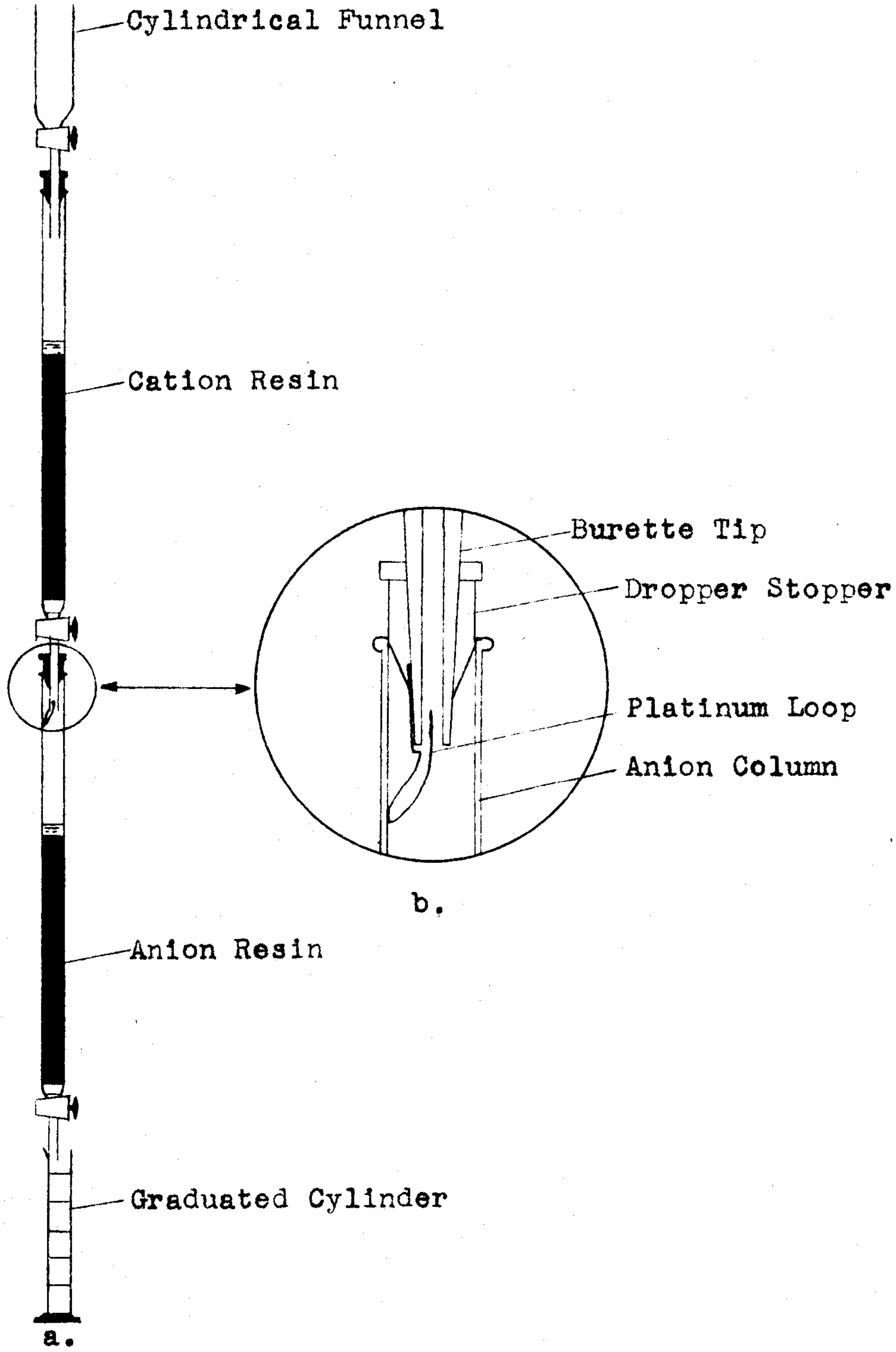
Apparatus:

The apparatus used in the absorption portion of these determinations consisted of two ion exchange columns placed one above the other as shown in Figure 14a. The upper column contains IR-120 in the acid form and the lower one contains IR-4B in the chloride form. To keep drops from falling from the tip of the upper burette into the lower one and disturbing the upper layers of resin, a two inch piece of platinum wire is slipped under the bottom edge of the eye-dropper stopper and then formed into an elongated loop at the tip of the burette (Figure 14b). The lower end of the loop touches the side of the burette and the liquid from the upper burette is conveyed to the side of the lower burette and runs down the wall in a continuous stream. By the use of this arrangement of tandem burettes, the phosphate ions are in a strongly acid solution for less than five minutes and there is little danger of hydration.

Procedure:

A 0.2000 gram sample of the mixed phosphates is weighed and dissolved in 50 ml. of water. This water solution is run through the column at 4 ml./min. This is followed by three 25 ml. portions of water at the same rate. The water insures removal of all of the phosphate from the cation column.

Figure 14 Apparatus for Cationic-Anionic Treatment of Phosphate Solutions



The cation column is removed and 500 ml. of 7% NaCl run through the anion column at 2 ml./min. This is titrated by the two end point method for orthophosphate content using 0.1N NaOH. The column is now eluted with 400 ml. of 5% HCl solution at 2 ml./min. The HCl fraction is boiled to hydrolyze the pyrophosphate. It is then neutralized to bromcresyl green using 18N NaOH. After being brought back to the acid color of the indicator with 0.5N HCl it is boiled for 15 minutes to remove any CO_2 which may have been present in the NaOH solution. After cooling, the solution is titrated with 0.1N NaOH.

When one of the ions is present in an amount less than 5%, the titration of the fraction containing this ion should be carried out using 0.02N NaOH to increase the sensitivity and accuracy of the method.

This procedure has been used on a number of synthetic mixtures of ortho- and pyrophosphates and the results are recorded in Table 18.

Table 18. Analyses of Ortho- Pyro Mixtures.
(% Given as % of Total P_2O_5 in Sample)

	Ortho		Pyro	
Mixture	Taken	Found	Taken	Found
A	18.2%	18.8%	81.8%	81.2%
		18.7		81.3
B	98.9	98.2	1.1	1.8
		97.7		2.3
C	0.93	1.5	99.07	98.5
		1.5		98.5

The percentage values reported in the table are readily found by hydrolyzing a sample of equal weight and titrating it for P_2O_5. The number of milliliters of base required in this total P_2O_5 titration is divided into the number of milliliters of base required to titrate the ortho fraction and the pyro fraction respectively.

The method appears to have an absolute accuracy of 1%. The only run having a greater deviation than 1% was the second run for the B mixture. The larger deviation here probably occurred in trying to weigh out 0.0035 gm. of $Na_4P_2O_7 \cdot 10H_2O$. This was overcome in the C mixture by making up a solution and taking an aliquot. The results show a precision of about 0.5%.

Since the question of the effect of high concentrations of NaCl on the titration of orthophosphate arose, a series of experiments to discover the effect, if any, were carried out. 0.2000 gm. samples of NaH_2PO_4 were dissolved in salt solutions having the concentrations noted in Table 19 and titrated by the two end point method. The data obtained are recorded in Table 19.

Table 19. Effect of NaCl on the Titration of Orthophosphoric Acid by the Two End Point Method.

Conc. NaCl	pH End Point 1	pH End Point 2	Ml. NaOH Used between the two end points
0	4.64	9.16	16.23
2	4.45	8.85	16.23
4.75	4.27	8.61	16.25
7	4.09	8.42	16.20
10	3.94	8.29	16.23
15	3.68	8.06	16.25

It is seen that the NaCl has no effect on the distance between the end points. The pH of the end point decreases as the concentration of NaCl is increased. These results are pictured graphically in Figures 15 and 16. Although the increased salt concentrations have no effect on the analytical results, the operator must be prepared to find his end point at a lower pH.

This method of analysis is designed to operate where only ortho- and pyrophosphates are present since the other phosphate ions will interfere. Experiments with trimetaphosphate show that it will appear in the ortho fraction while triphosphate is almost quantitatively retained by the resin and comes off with the pyro fraction. Phosphate glasses will for the most part not be absorbed and can be found in the spent phosphate solution. It does seem possible that condi-

Figure 15 Effect of NaCl on H_3PO_4 Titration Curve

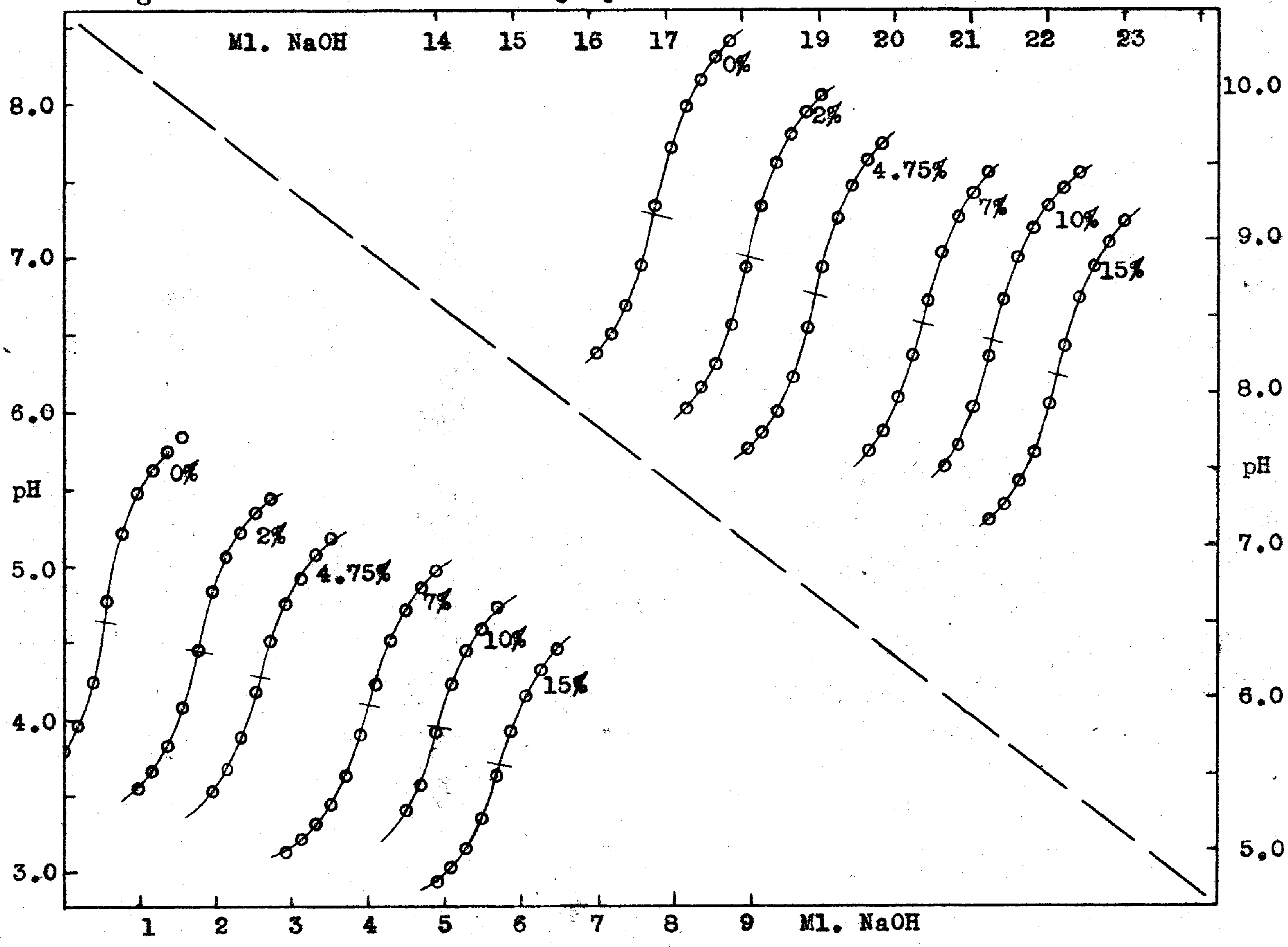
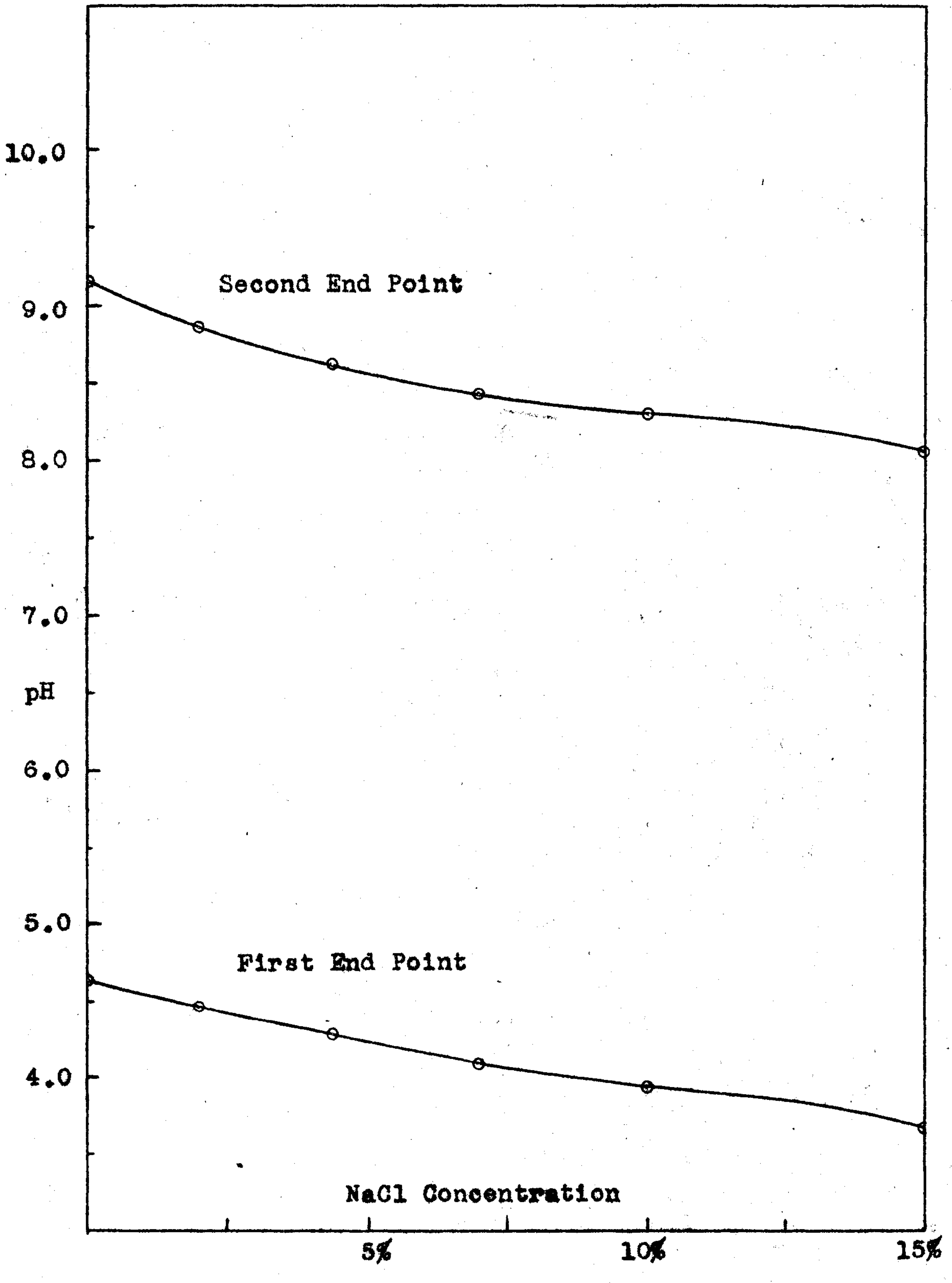


Figure 16 Effect of NaCl on End Point pH



tions might be found to remove the trimeta with the ortho and triphosphate with the pyro.

5. Conclusions.

After careful consideration of the data presented, the following conclusions may be drawn:

a. Orthophosphate can be quantitatively separated from pyrophosphate and the amounts of each present in a mixture can be determined with a 1% accuracy. This is accomplished by using the weak anion exchange resin in the chloride form with NaCl and HCl elutrient solutions.

b. Hydroxyl ion is such a strong elutrient on the weak resin that the various phosphates are all removed at the same rate.

c. Trimetaphosphate and the metaphosphate glasses are poorly absorbed on IR-4B in the hydroxyl probably indicating a similarity in their reacting groups.

d. The strong anion exchange resin (IRA-400) in the hydroxyl form is not useful for separation of the phosphates because it absorbs trimetaphosphate and the phosphate glasses so strongly that they are removed only incompletely and in decomposed form.

e. A tendency to separate is shown by ortho-, pyro- and triphosphate ions when absorbed and eluted with NaOH solution.

f. If a mixture of the ions: ortho-, pyro-, tri-, and trimetaphosphate were absorbed on IR-4B they would be removed in the order: (1) ortho, (2) trimeta, (3) pyro, and (4) tri.

g. The reaction on a weak anion exchange resin appears to be a true exchange because a dilute NaOH solution will remove an equivalent amount of phosphate from the resin.

VI Titration with the High Frequency Analyzer.

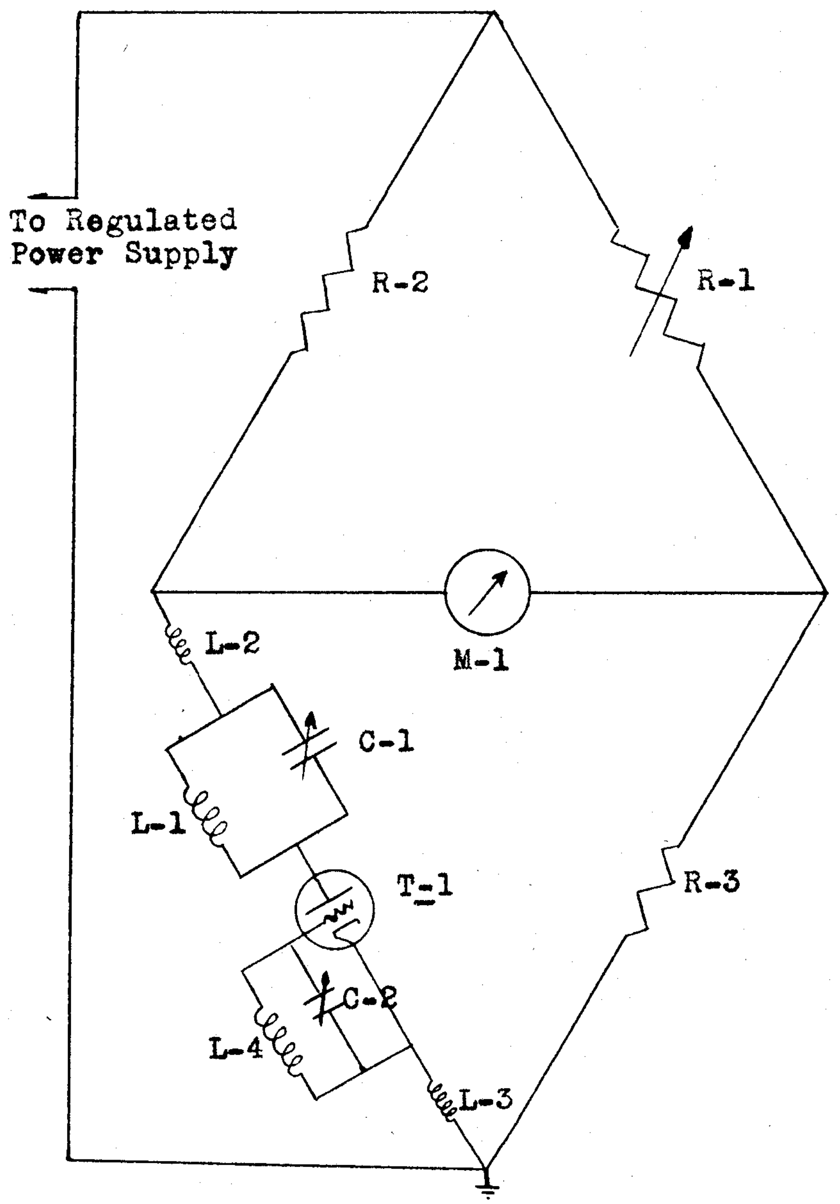
A. Apparatus.

A simplified diagram of the apparatus is shown in Figure 17. It is essentially a Wheatstone Bridge type of circuit in which the lower left arm contains a radio frequency oscillator. This arm contains radio frequency chokes (L-2 and L-3) which confine the high frequency currents to this arm of the bridge and allow only direct current to flow out into the remainder of the circuit.

The oscillator coil (L-1) has a diameter of 60 mm. and a glass vessel can be placed inside this coil. The circuit is then tuned for manimum deflection, to the right of the microammeter (M-1). The bridge circuit is then balanced by adjusting the potentiometer (R-1) until the microammeter gives a zero reading. As sodium hydroxide or some other titrating solution is added, the coil will be loaded to a different degree and the current through the lower left arm will change. This of course causes a change in the reading of the microammeter. When these meter readings are plotted against milliters of reagent added, straight line plots are obtained. The intersections of the straight lines give the end points of the titrations.

The conductivity titrations were made using a dip type conductivity cell with a cell constant of about one. A Conductivity Bridge, Model RC-1B, manufactured by Industrial Instruments Incorporated, was used to determine

Figure 17 Simplified Analyzer Circuit



the resistance of the solution. The reciprocal of the resistance, i. e. conductance, was calculated and this value was plotted against milliliters of base added.

Since no provision could be made to thermostat the solution in the high frequency analyzer cell, all titrations, analyzer and conductance, were carried out at room temperature.

B. Procedure

0.2 gm. samples (anhydrous basis) of the various sodium phosphates were dissolved in water and stirred with 30 ml. of the cation exchange resin, IR-120, in the acid form. The solution of the phosphoric acid was separated by filtration, and the resin was washed until a total volume of 200 ml. was obtained. This solution was placed in the coil of the high frequency analyzer and titrated with 0.1N NaOH. Samples for conductometric titration were prepared in the same manner.

C. Data and Discussion.

The microammeter readings were plotted against milliliters of base added, and lines were drawn through the points. These plots are shown in Figures 18 to 21. The conductance curves are drawn on the same graph as the analyzer curves in order that a comparison of the sharpness of the breaks can readily be made. The curves are also plotted in such a way that the conductance and analyzer curves have about the same overall height. This procedure makes possible a significant comparison of the breaks.

The orthophosphoric acid curves are shown in Figure 18. Both of these curves have no breaks in the strong acid portion but a very sharp one is present when the strong acid group is completely neutralized. Both curves show a break when the second acid group is neutralized and the breaks seem to be of about the same magnitude. The conductance curve shows no evidence of the neutralization of the third acid group, but the analyzer curve shows a definite break. This third break is at the point where the third acid group is neutralized.

In Figure 19 the curves for pyrophosphoric acid are presented. The weak acid portions of these curves are nearly the same, and the breaks are roughly of the same magnitude. The strong acid portions of the curve on the other hand differ considerably. The strong acid portion

Figure 18 Titration Curves, H_3PO_4 vs NaOH

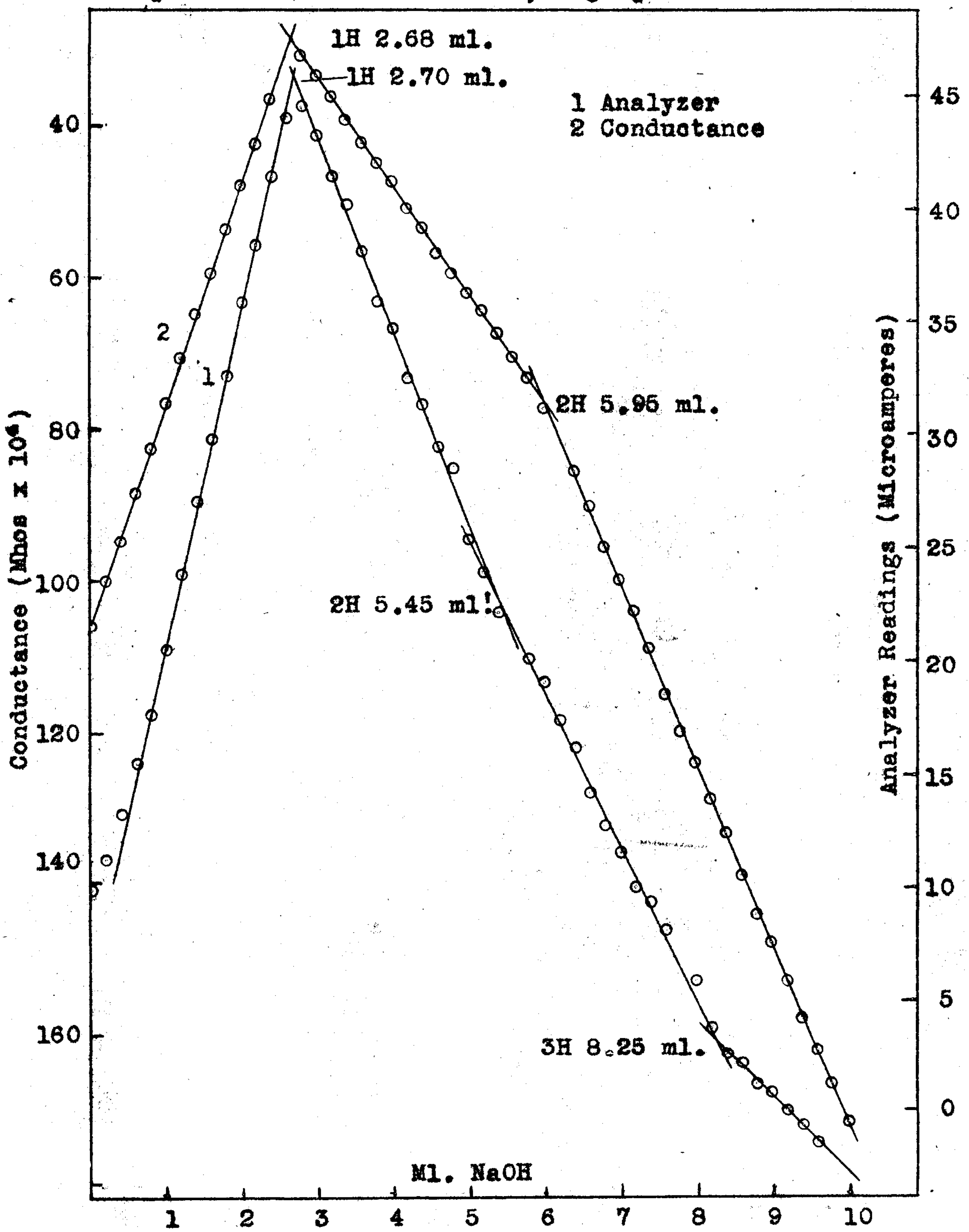
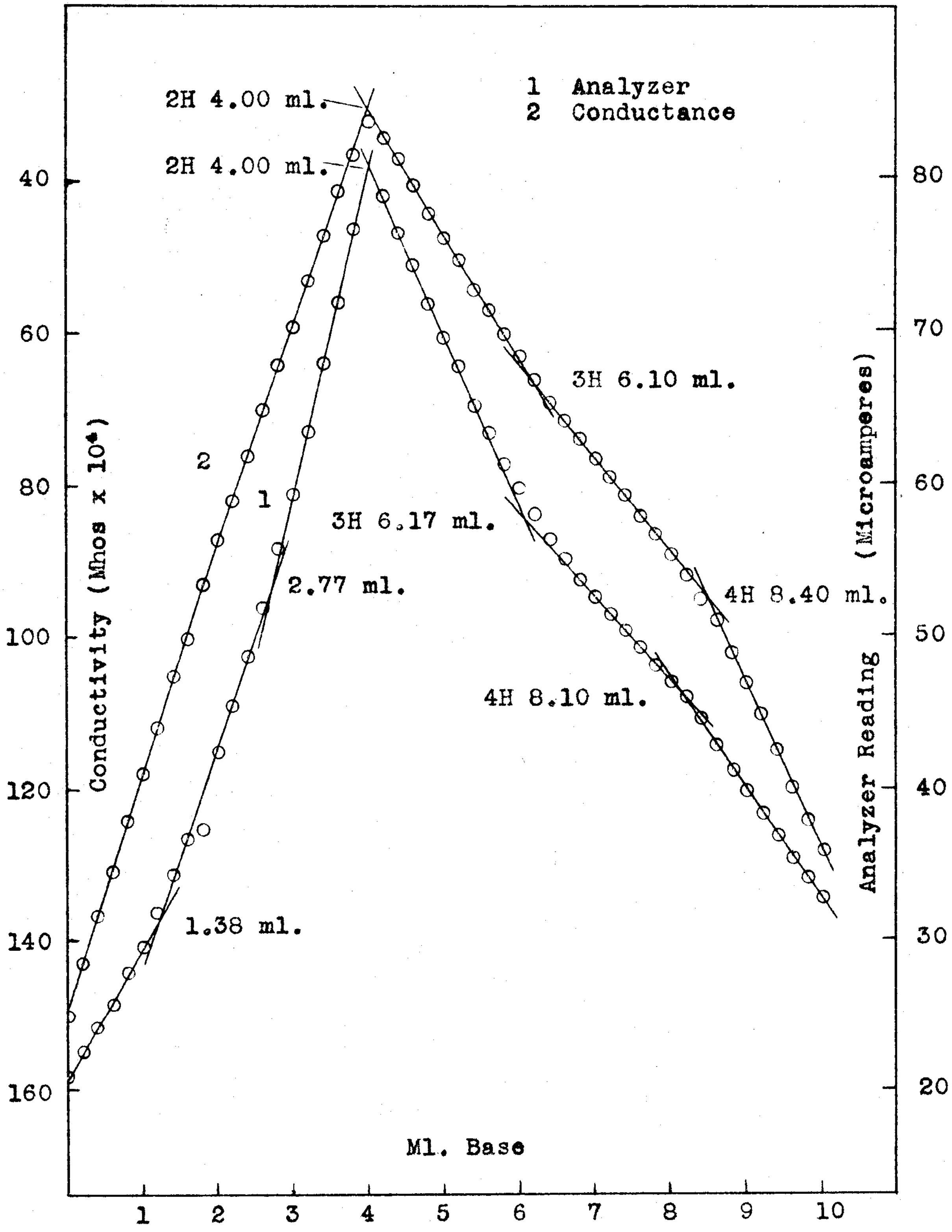


Figure 19 Titration Curves, $H_4P_2O_7$ vs NaOH



of the conductance curve is nearly straight and exhibits only slight curvature. The analyzer curve shows two rather distinct breaks. The number of milliliters of base used between the successive breaks is about the same.

The curves for triphosphoric acid are reproduced in Figure 20. It is readily seen that a situation similar to that found for pyrophosphoric acid exists. The weak acid portions of the curve are nearly the same, though the analyzer may give slightly sharper breaks. The strong acid portion of the conductance curve is again nearly a straight line. The strong acid portion of the analyzer curve now has four straight sections all nearly equal in length. Again there is one more straight section in the strong acid portion than there are strong acid groups in the molecule.

The trimetaphosphoric acid plots are presented in Figure 21. The conductance curve again shows the slight tendency to break in the strong acid portion of the curve, but with this exception the curves are strictly those obtained for a strong acid like HCl and a strong base such as NaOH. The analyzer shows no indication at all of differentiating between the strong acid groups of the molecule.

Figure 20 Titration Curves, $H_6P_6O_{18}$ vs NaOH

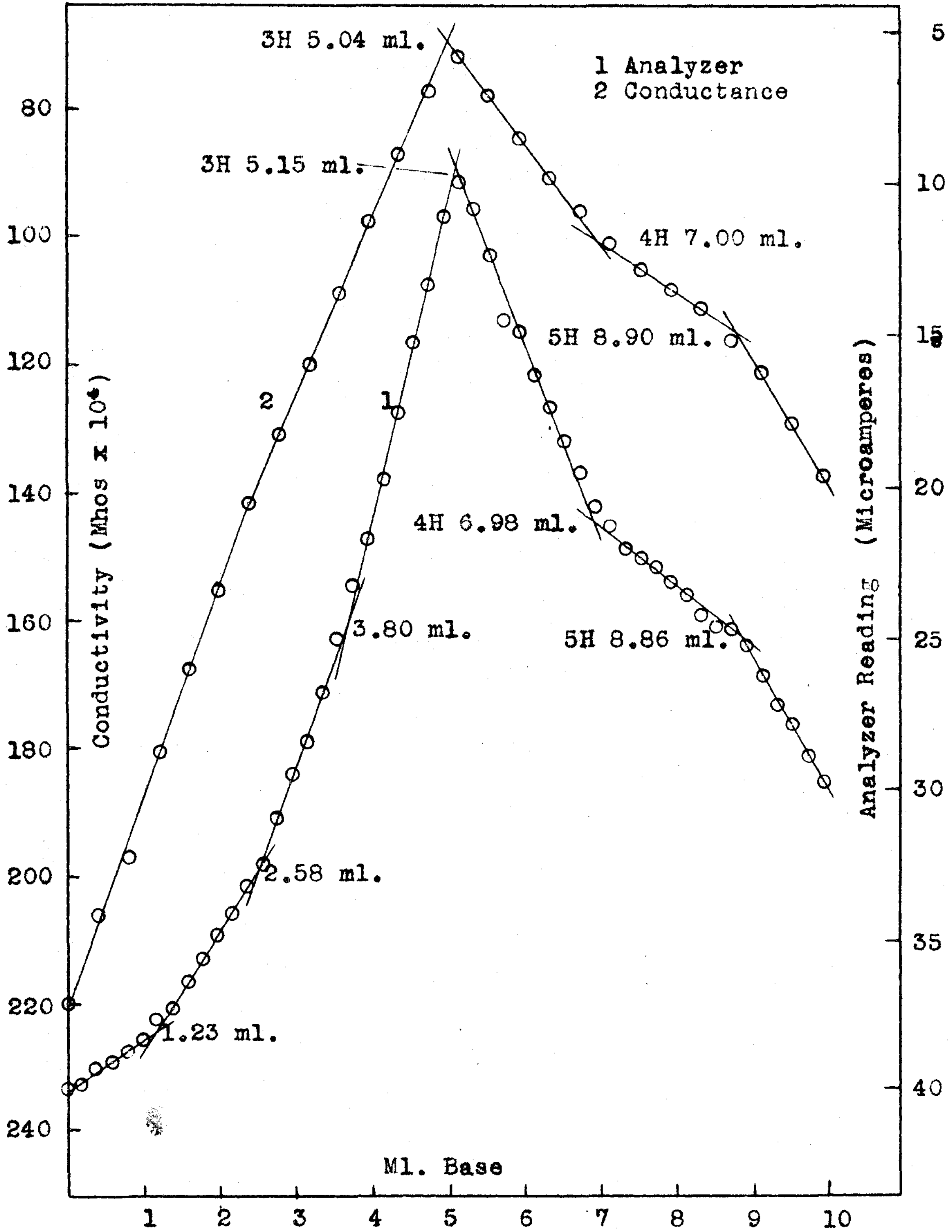
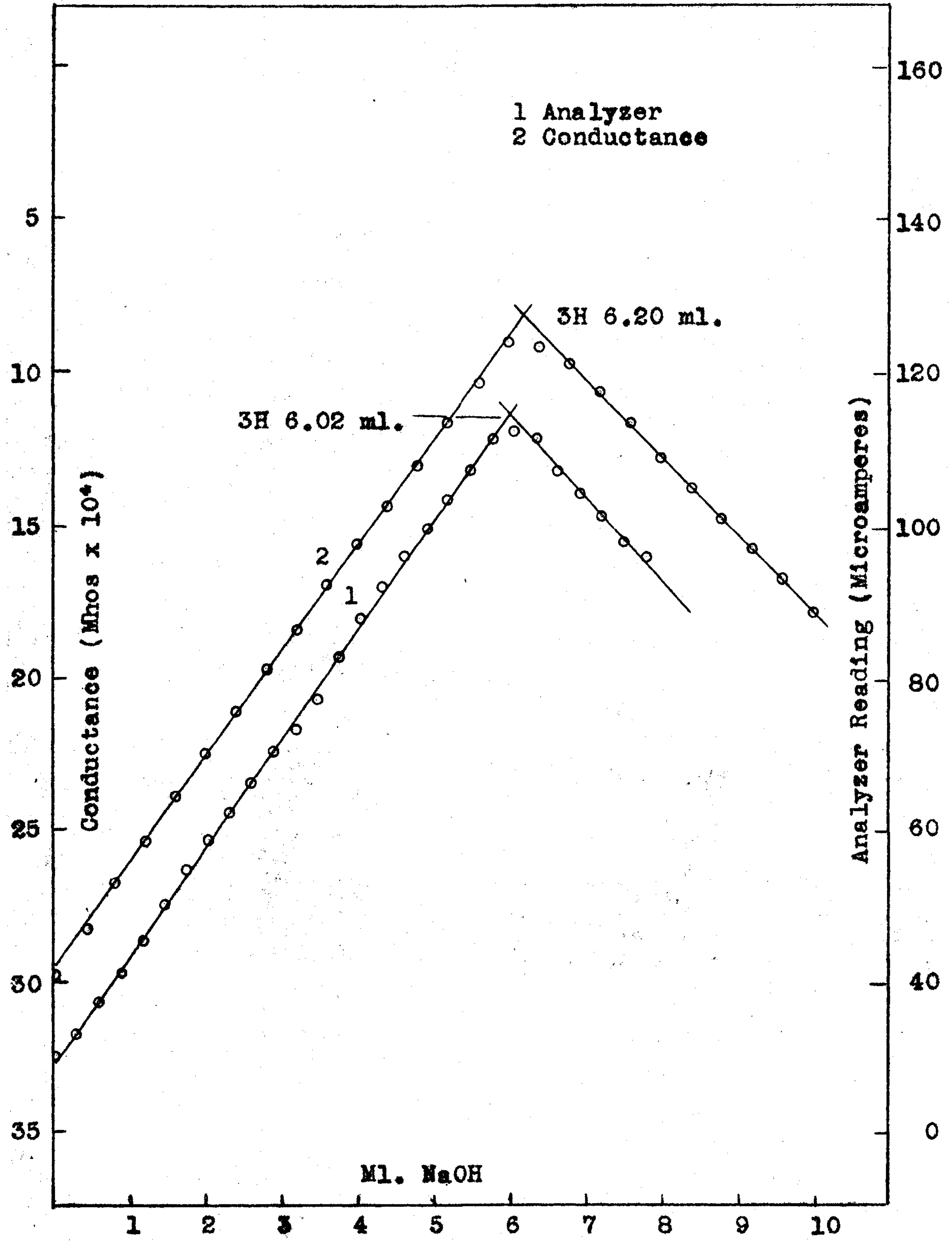


Figure 21 Titration Curves, $H_5P_3O_9$ vs NaOH

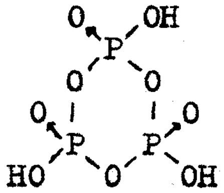


D. Conclusions.

The high frequency analyzer data available are not complete because the instrument used tended to be unstable and in some cases curved lines instead of straight ones were obtained. The curves presented have been duplicated with only minor variations in slope. Due to the instability of the instrument it was often necessary to run a considerable number of curves in order to get several which would check. In spite of mechanical difficulties it seems reasonable to state the following conclusions:

1. The completion of the neutralization of the third acidic hydrogen on H_3PO_4 can be detected with this instrument.

2. All three hydrogens on $H_3P_3O_9$ are strong and of equal acidity. Added support is given to the proposed cyclic structure:



3. The weak acid portions of the analyzer curves appear essentially to be conductance curves (except in the case of H_3PO_4) since they parallel the conductance curves so closely.

4. The breaks in the strong acid portion of the pyro- and triphosphoric acid analyzer curves indicate that the

process taking place is not merely a replacement of ionized hydrogen ions with ionized sodium ions. The acid molecule itself must be undergoing some change. The most likely change is complexing of the sodium ions to change the dipole moment of the molecule and hence the effect on the analyzer.

VII. Summary

The Samuelson average chain length of a "metaphosphate" glass increases as the length of time of heating and the temperature of preparation are increased. A method has been devised for the measurement of the amount of combined water in a glass and the excess Na_2O. Use of this method shows that as the temperature of preparation is increased, the amount of excess Na_2O increases, indicating a loss of P_4O_{10} and at the same time the amount of combined water decreases giving, under the experimental conditions used, a net increase in Samuelson average chain length. The so-called "metaphosphate" glasses are best represented by a polyphosphate formula having the empirical form: $(NaPO_3)_{\bar{n}}(H_2O)_x(Na_2O)_{1-x}$, where $\bar{n}$ is the Samuelson average chain length. "Metaphosphate" glasses can absorb most of their combined water from the atmosphere.

The "metaphosphate" glasses are not exclusively linear polymers, as assumed by Samuelson, but appear to contain either rings or branches. Present evidence indicates that branching occurs.

An analytica procedure has been devised for the determination of ortho- and pyrophosphates in mixtures of the ions. This method depends on the absorption of the ions on the weak anion exchange resin IR-4B in the chloride form. Orthophosphate is then removed by eluting with 7% NaCl solution and the pyrophosphate with 5% HCl solution. The amount of the ions present is determined by the two end point titration method. A precision of 0.5% and an accuracy of 1% are obtained. The other phosphates will interfere with this determination. Trimetaphosphate appears in the ortho fraction and triphosphate in the pyro fraction.

Batchwise operations with the weak anion exchange resin indicate that if ortho-, pyro-, tri- and trimetaphosphoric acids are absorbed on the resins, the proper conditions should cause their elution in the following order: ortho-, trimeta-, pyro- and triphosphoric acids. The latter two behave so much alike that their separation will be very difficult.

Ortho-, pyro- and trimetaphosphates are removed at the same rate when absorbed on IR-4B in the hydroxyl form and the column eluted with NaOH solution. Trimetaphosphate and the "metaphosphate" glasses are incompletely absorbed by this resin.

The strong anion exchange resin in the hydroxyl form absorbs all the phosphate ions quantitatively. Ortho-, pyro- and triphosphates show some tendency to fractionate on this resin when eluted with NaOH solution. Trimetaphosphate and the "metaphosphate" glasses are removed for the most part only after being hydrated.

Experimental titration curves for ortho-, pyro, tri- and trimetaphosphoric acids with NaOH, have been prepared using the high frequency analyzer and also a conductance bridge. The weak acid portions of the curves are very similar for both types of measurements except in the case of orthophosphoric acid. The high frequency analyzer curve has a break where the third hydrogen of H_3PO_4 is neutralized. This break is not present in the conductivity curve and does not show up in pH titrations. The similarity of the analyzer and conductance weak acid titration curves indicates that the high frequency analyzer may be measuring conductances in this region. The lack of breaks in the strong acid portion of the trimetaphosphoric acid curve with the high frequency analyzer gives support to the previously proposed cyclic formula. The strong acid portions of the analyzer curves for pyro- and triphosphoric acids show an extra break which cannot be explained by the evidence on hand. Since these two ions are complex formers, the extra break may be due to this complexing ability. The conductance curves are smooth in the strong acid portion for all ions.

VIII Suggestions for Future Work.

The field of phosphate chemistry is ripe for a great variety of investigations, but the one portion of the field which seems to be in the greatest need, and the one which must be conquered before all others, is that of analytical methods. A number of methods have been proposed but they all have short comings when applied to complex mixtures of the ions. A truly reliable method would be a great advance.

There are several extensions which could be made on the work described in this paper. "Metaphosphate" glasses should be prepared at temperatures above 950°C and analyzed by the crystallization method to show that Karbe and Jander's decrease in anionic weights is due to the loss of P_4O_{10} from the melt.

Titrations should be carried out on pyro- and triphosphoric acids with the high frequency analyzer to show whether the strange break in the strong acid portion of the curve is dependant on concentration. Mixtures of the ions might be titrated to determine whether individual ions may be detected in the strong acid portion of the curve.

Investigations should be extended on the use of ion exchange resins to separate the phosphate ions. This might especially be applied to the quantitative non-absorption of glasses and the separation of ortho- and trimetaphosphates from pyro- and triphosphates. The amounts of the individual ions in the two mixtures could then be determined by titrating each fraction before and after hydrolysis.

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