[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

An Ion-exchange Purification of Sodium Tetrametaphosphate[1a]

BY DUANE L. BARNEY AND JOHN W. GRYDER[1b]

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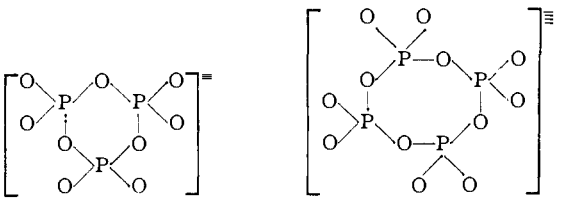
A method of preparing pure sodium tetrametaphosphate involving anion exchange on Dowex 1 and elution with various cations is reported. Proof of purity consists of analytical data, titration curves, solubility data, X-ray diffraction and enzymatic analysis.

Introduction

The polymetaphosphoric acids, $(HPO_3)_n$, and their salts have been the object of numerous studies in the past but as yet few quantitative experiments have been performed on well characterized preparations.[2-4] This is partially because much of the work has been oriented toward industrial application of the compounds as sequestering agents, for which purpose the poorly characterized high molecular weight metaphosphates are most effective. In addition, the methods of preparation are such that impurities are almost certainly present. With few exceptions, the methods of preparation are so similar that the product is contaminated not only with other metaphosphates, but also with ortho-, pyro- and polyphosphates. Purification is complicated by the fact that the main product has chemical properties which are very similar to those of the impurities.

The structures of the tri- and tetrametaphosphates have been determined by X-ray studies[5-7] which establish the following structures for the ions



The colligative properties of solutions of metaphosphates have also been used to determine the degree of polymerization, but the high charge on the ions makes work of this sort ambiguous and has resulted in different workers obtaining contradictory data.

The present experiments were undertaken to obtain pure metaphosphates in order to clarify conflicting statements concerning the chemical properties of the compounds. In view of the similarity of the metaphosphates, ion-exchange methods were chosen to effect a separation. Rieman and coworkers[8] have studied an ion-exchange separation of condensed phosphates. However, no attempt was made to isolate the product or to prove the purity of the material.

Materials and Methods

Ion-exchange Resins.—Dowex 1, a product of the Dow Chemical Company, and Amberlites IRA 410, IR 4B and IR 120 made by Rohm and Haas, were employed in the following experiments. The nitrate form of the resins was prepared by eluting with 3 *f* nitric acid,[9] saturated sodium nitrate, and finally with water. The chloride form was prepared by first converting the resin to the nitrate form and then eluting with 3 *f* hydrochloric acid, 5 *f* sodium chloride and then with water. The hydroxide form of IRA 410 was prepared by washing with carbonate free 2.5 *f* NaOH. The acid form of IR 120 was made by washing with 6 *f* HCl.

Metaphosphates.—Sodium tetrametaphosphate was prepared by first making the copper salt and then metathesizing with sodium sulfide.[10] To make the copper tetrametaphosphate, 19.89 g. of finely powdered CuO, added in small amounts, was first mixed with 35.5 ml. of 85% orthophosphoric acid in a platinum dish. The mixture was stirred with an electric stirrer until the CuO was completely dissolved and the mixture had changed to a light blue, viscous paste. The complete operation required about three hours. One-half ml. of carrier free $H_3P^{32}O_4$ obtained from Oak Ridge, containing about 3 millicuries of radio phosphorus and 0.077 *f* in HCl, was added to the starting mixture. Ten drops of concentrated nitric acid were used to hasten solution of the cupric oxide. After the formation of the characteristic light blue color, the material was heated at 100° for two hours and then at 450 ± 15° for 24 hours, at which time the product was light green in color. After washing the green sample with water several times, the copper tetrametaphosphate was converted to the sodium salt by slowly adding 5 g. of the powdered copper salt to 5.4 g. of $Na_2S \cdot 9H_2O$ dissolved in 43 ml. of water. After filtering off the copper sulfide, the sodium tetrametaphosphate was precipitated by slowly adding an equal volume of absolute ethyl alcohol with constant stirring. Material prepared in this fashion was used for the impure tetrametaphosphate in the subsequent work.

Sodium trimetaphosphate was prepared by heating a mixture of 60 g. of $Na_2HPO_4 \cdot 12H_2O$ and 17 g. of NH_4NO_3 at 300 ± 15° for six hours.[11] $Na_2HP^{32}O_4$ was prepared by adding 1/2 ml. of the $H_3P^{32}O_4$ from Oak Ridge to a solution containing 5 g. of $Na_2HPO_4 \cdot 12H_2O$ and neutralizing the solution to the phenolphthalein end-point with sodium hydroxide. The solution was then evaporated slowly under an infrared lamp. A small portion of this material was included in the 60 g. of disodium hydrogen phosphate. Material prepared in this manner was used for impure sodium trimetaphosphate in the subsequent work.

Tetramethylammonium Hydroxide.—The quaternary ammonium hydroxide was prepared from Matheson, Coleman and Bell tetramethylammonium bromide by shaking a solution of the reagent with carbonate-free silver oxide.

Counting Equipment.—A continuous automatic recording of the radioactivity was obtained by passing the effluent solution through an annular Geiger–Müller tube connected to a Nuclear Instrument model 165 scaling unit which in turn transmitted impulses to a Nuclear Instrument count rate meter model 1014. The count rate meter was connected to an Esterline–Angus recorder which continuously recorded the counting rate. In order to accentuate small peaks of activity, the data were recalculated in terms of minutes per count.

(1) (a) This work was supported in part by research grant G-3604-(C), from the National Institutes of Health, Public Health Service. Based on a dissertation submitted by Duane L. Barney in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) Person to whom inquiries should be addressed.

(2) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1944, pp. 210–224.

(3) B. Topley, *Quart. Rev.*, **3**, 345 (1949).

(4) K. Karbe and G. Jander, *Kolloid-Beihefte*, **54**, 1 (1942).

(5) L. C. Pauling and J. Sherman, *Z. Krist.*, [A] **96**, 481 (1937).

(6) V. Caglioti, G. Giacomello and E. Bianchi, *Atti accad. Italia Rend.*, [7] **3**, 761 (1942).

(7) C. Romers, J. A. A. Ketelaar and C. H. MacGillavry, *Acta Cryst.*, **4**, 114 (1951).

(8) J. Beukenkemp, W. Rieman, III and S. Lindenbaum, *Anal. Chem.*, **26**, 505 (1954).

(9) Concentrations will be expressed in volume formality, *f*, the number of formula weights per liter of solution.

(10) F. Warschauer, *Z. anorg. Chem.*, **36**, 137 (1903).

(11) G. von Knorre, *ibid.*, **24**, 369 (1900).

Experimental Results

Purification.—Preliminary results indicated that the tri- and tetra-metaphosphates were adsorbed on both the chloride and nitrate forms of each of the three anion-exchange resins used. However, activity measurement with a survey meter indicated that the band with Dowex 1 was narrower. This was probably due to the fact that Dowex 1 of 100–200 mesh was used while the other resins were 20–60 mesh. Dowex 1 was therefore used in subsequent experiments. It was also determined that the column did not "bleed" or exchange appreciably with the carbon dioxide present in the distilled water upon prolonged washing.

Since metaphosphates are known to form complexes with various cations, the method of approach was to adsorb the metaphosphates on the column and then make use of differences in dissociation constants of complexes to remove the metaphosphates and to separate them. Investigation of the literature on the instability constants of metaphosphate complexes[12] indicated that the cation with the greatest difference in complex constants for tri- and tetrametaphosphates, consistent with ease of separation of the cation from a phosphate-containing eluate was nickelous ion. A series of experiments with nickel nitrate as elutriant was performed using 5 mg. each of sodium tri- and tetrametaphosphate on a nitrate column 200 mm. long and 10 mm. in diameter with a flow rate of 1 ml./cm.^{2}/min. A separation of the two metaphosphates was obtained using 0.085 f $Ni(NO_3)_2$. After the second peak was through the column 3 f HNO_3 was added and a third peak was obtained, indicating that the original samples contained impurities which were not removed from the column with nickel ion.

The samples obtained by the nickel nitrate treatment, however, were impure as was evidenced by the fact that a precipitate formed in the solution from the leading edge of the first peak. The elimination of this impurity was accomplished by eluting with magnesium nitrate, which removed the interfering substance but was not effective in separating the tri- and tetrametaphosphates. Figure 1 shows the results of a separation performed by a combination of magnesium nitrate and nickel nitrate elutions. The second nickel peak was shown to be trimetaphosphate by doing an elution identical to that just mentioned with the exception that the specific activity of the trimetaphosphate was increased.

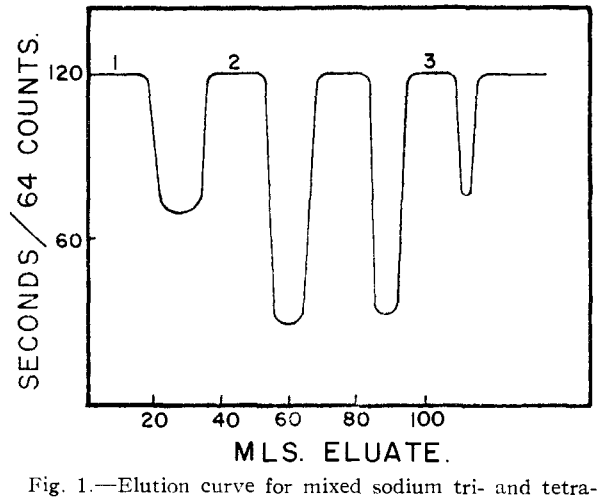


Fig. 1.—Elution curve for mixed sodium tri- and tetrametaphosphate; elutriants: 1, 0.025 f $Mg(NO_3)_2$; 2, 0.085 f $Ni(NO_3)_2$; 3, 3 f HNO_3.

(12) H. W. Jones, C. B. Monk and C. W. Davies, *J. Chem. Soc.*, 2693 (1949); H. W. Jones and C. B. Monk, *ibid.*, 3475 (1950).

In order to obtain larger samples of material the size of the resin column was increased so that several grams of material could be employed. The separation was still satisfactory. Experiments with tri- and tetrametaphosphate alone indicated that both preparations contained several impurities which were separated from the bulk of the sample. From the activity of the various impurities it appears that the tri- and tetrametaphosphates each contained approximately 15% impurity.

Several methods of separating the metaphosphates from the nickel eluate were tried. Precipitation of the nickel with hydrogen sulfide or with sodium hydroxide failed because essentially all of the metaphosphate coprecipitated with the nickel. The method finally adopted was to precipitate the metaphosphates with lead and then metathesize with a sodium sulfide solution. The lead metaphosphates were obtained by adding an equal volume of 1 f lead nitrate to the nickel eluate containing the desired metaphosphate. Precipitation was very slow requiring 12 hours for completion. For the metathesis with sodium sulfide, 20 g. of the finely powdered lead salt was suspended in 80 ml. of water and a solution of 15.5 g. of $Na_2S \cdot 9H_2O$ dissolved in 50 ml. of water added dropwise until the solution remained slightly basic. After filtering the mixture, the sodium salt was precipitated by adding an equal volume of absolute alcohol. The sodium salt was reprecipitated several times by dissolving the sample in a minimal quantity of water and precipitating with an equal volume of absolute alcohol.

The time required for column treatment and precipitation of the metaphosphates would be expected to result in some hydrolysis of the salts. Titration curves for the neutralization of the tetrametaphosphoric acid with tetramethylammonium hydroxide indicated that a small amount of weak acid was present in the preparation. A Beckman Model G pH meter was used for the measurements. The tetrametaphosphoric acid was prepared by passing a solution of the sodium salt through the acid form of Amberlite IR 120. The small amount of weak acid impurity was removed from the tetrametaphosphate by precipitation with silver ion. The sodium tetrametaphosphate was dissolved in a minimal amount of water and enough 1 f $AgNO_3$ was added to give one gram atom of silver ion for each 10 gram atoms of phosphorus in the sample. The mixture was filtered and the silver ion remaining in solution precipitated by adding an amount of 1 f Na_2S equivalent to the total amount of silver ion added. The sodium tetrametaphosphate was precipitated after filtration by adding an equal volume of absolute alcohol. The salt was reprecipitated with alcohol once. The titration curves for

the partially purified and silver-treated tetrametaphosphates are given in Figs. 2 and 3.

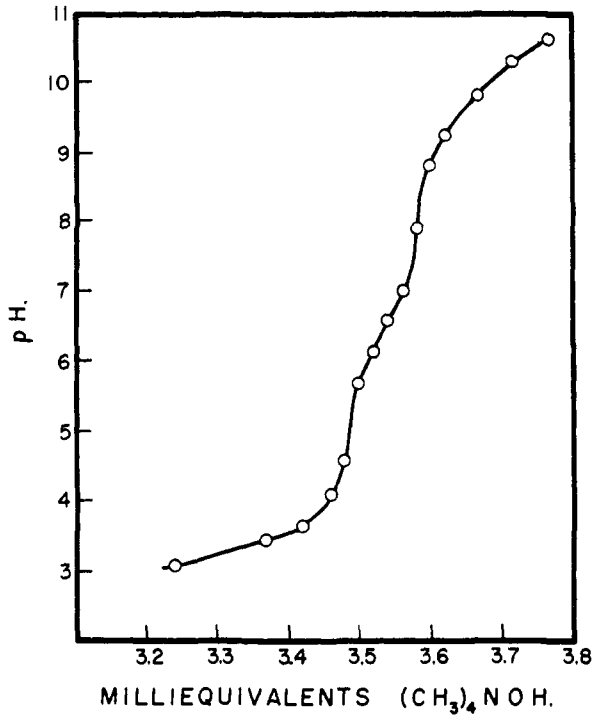


Fig. 2.—Titration curve for partially purified sodium tetrametaphosphate.

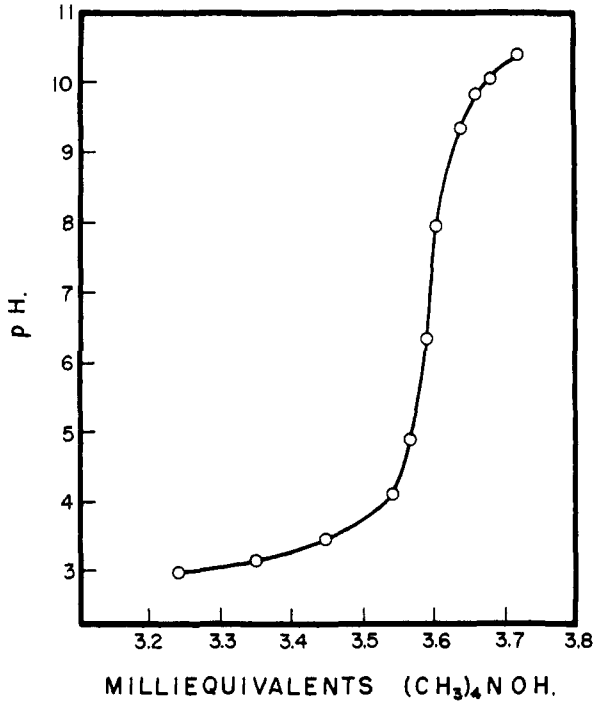


Fig. 3.—Titration curve for purified sodium tetrametaphosphate.

Proof of Purity.—Considerable difficulty is encountered in proving the purity of a compound in which the chemical behavior of possible impurities is closely related to the desired product. Therefore it is necessary to test the material by as many independent methods as possible. In the present case, the titration curves for the tetrametaphosphoric acid as indicated in Fig. 3 suggest the absence of ortho-, pyro- or polyphosphates in the product.

The sodium salt was analyzed for water, phosphorus and sodium. The water content was determined by the loss of weight after heating to constant weight at 1000°. The phosphorus content was determined after conversion to orthophosphate by boiling in 6 *f* HCl for 4 hours. The magnesium ammonium phosphate procedure was used with one reprecipitation.[13] Analyses for sodium were carried out by passing a solution of the sodium salt through the hydroxide form of an Amberlite IRA-410 column and titrating the eluate with standard HCl to the methyl orange end-point. The results of these analyses agreed to within 0.1% with the theoretical values for $Na_4P_4O_{12}\cdot 4H_2O$. These analyses, however, do not prove the purity of the sample because no distinction can be made between polymers and because any phosphate with a sodium to phosphorus ratio of 1:1 would give comparable data. Indeed, analyses on the partially purified samples which gave titration curves similar to those in Fig. 2 agreed with the theoretical values as well as the more highly purified product.

The method of constancy of solubility[14] has been most valuable in the much more complex field of protein chemistry and is capable of detecting the presence of impurities closely related to the bulk of the product. This method was therefore employed in the present investigation. The apparatus described by Reilly and Rae[14b] was used. The solvent was a 30 volume % ethanol–water solution. The amount of sodium tetrametaphosphate which dissolved was determined by counting the disintegration of the radiophosphorus in the filtered solution with a Geiger–Müller dipping solution counter. The results are shown in Fig. 4 and indicate that the sample is pure to within the 1.5% experimental error.

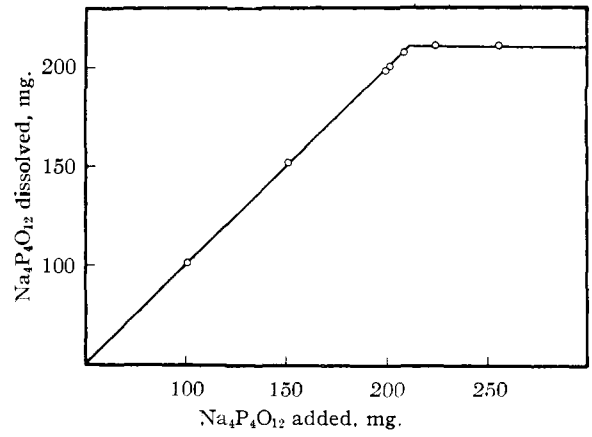


Fig. 4.—Solubility curve for purified sodium tetrametaphosphate.

(13) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, pp. 546–547.

(14) (a) R. M. Herriot, *Chem. Revs.*, **30**, 413 (1942); (b) J. Reilly and W. N. Rae, "Physico-Chemical Methods," Vol. I, Methuen and Co., Ltd., London, 1954, pp. 378–383.

X-Ray diffraction was used to determine the unit cell dimensions of sodium tetrametaphosphate. Single crystal precession pictures taken with Cu Kα radiation yielded the following monoclinic cell dimensions: $a = 9.65 \pm 0.04$ Å., $b = 12.32 \pm 0.04$ Å., $c = 6.17 \pm 0.04$ Å., $\beta = 92°30' \pm 10'$. The systematic absences are $h0l$ with h odd and $0k0$ with k odd; they determine uniquely the space group $P_{2_1/a}$. The density is 2.18 ± 0.01 g./cm.^{3} found by the pycnometric method using toluene. Assuming the unit cell contains $2(Na_4P_4O_{12}\cdot 4H_2O)$, the calculated density is 2.173 ± 0.006 g./cm.^{3}. These data are in agreement with those of Andress, *et al.*[15]

Since the unit cell contains 8 PO_3 groups, the trimetaphosphate is ruled out. Dimetaphosphate is impossible because of the predicted low stability of such a compound. X-Ray powder pictures of $Na_2HPO_4\cdot 12H_2O$, NaH_2PO_4, Na_3PO_4 and $Na_4P_2O_7$ were compared with powder pictures of the $Na_4P_4O_{12}\cdot 4H_2O$. There was no indication of any of these compounds as impurities in the sodium tetrametaphosphate.

As a final test for the absence of pyro- and tripolyphosphate an enzymatic method was employed. Rat kidney contains an enzyme or enzymes which hydrolyze lower polyphosphates to orthophosphate at *p*H 8 and 36°. Sodium tetrametaphosphate was incubated for 2 hours with rat kidney extract prepared from freshly killed Wistar rats. The orthophosphate liberated was determined by the molybdenum blue method of Lowry and Lopez.[16] Less than 0.2% of the phosphorus was hydrolyzed to orthophosphate. That the metaphosphate was not acting as an inhibitor to the enzymatic reaction was shown by determining the extent of hydrolysis of added pyrophosphate in the presence of metaphosphate.

The titration curves and enzymatic analysis establish the absence of hydrolysis products or polyphosphates in the sample. The fact that the ion-exchange column effects a complete separation of the tri- and tetrametaphosphates proves the absence of trimetaphosphate in the final product and strongly indicates that other metaphosphates would be absent. The solubility indicates that indeed only one material is present and the X-ray work establishes the product as sodium tetrametaphosphate.

Acknowledgments.—We are indebted to Professor J. D. H. Donnay and Dr. Gabrielle Donnay for supervision of the X-ray work. Mr. Robert J. Gross performed the solubility experiments. In addition, Mr. Gross and Miss Ella Ball were of considerable assistance in all phases of the work. One of us (D. L. B.) was the recipient of a du Pont Fellowship for the academic year 1952–1953, and of a grant-in-aid from the Hynson–Westcott and Dunning Fund for the academic year 1951–1952.

(15) K. R. Andress, W. Gehring and K. Fischer, *Z. anorg. Chem.*, **260**, 331 (1949).

(16) O. H. Lowry and J. A. Lopez, *J. Biol. Chem.*, **162**, 421 (1946).

[CONTRIBUTION NO. 373 FROM THE INSTITUTE FOR ATOMIC RESEARCH, DEPARTMENT OF CHEMISTRY, AND VETERINARY MEDICAL RESEARCH INSTITUTE, IOWA STATE COLLEGE]

Kinetics of the Reduction of Ferric Ion by Hydroquinone in the Presence of 1,10-Phenanthroline[1]

BY FREDERICK R. DUKE AND FRANK R. PARCHEN

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The reduction of ferric ion by hydroquinone in the presence of 1,10-phenanthroline is found to proceed by direct complexing of the hydroquinone by the ferric ion in competition with the 1,10-phenanthroline. This mechanism is in contrast to that generally believed to be operative when the iron–1,10-phenanthroline complex acts as indicator, there being no displacement of 1,10-phenanthroline in the latter process.

Hydroquinone is often used as the reducing agent in the colorimetric determination of iron with 1,10-phenanthroline and in some procedures is added simultaneously or immediately preceding the addition of 1,10-phenanthroline to a ferric solution. This kinetic study was undertaken for the purpose of determining the effect, if any, that the presence of 1,10-phenanthroline might have on the rate of reduction of ferric ion by hydroquinone.

When the ferrous or ferric 1,10-phenanthroline complex is used as an indicator, no loss of 1,10-phenanthroline occurs from the complex. In the oxidation or reduction of the indicator, the electrons apparently are transferred in and out of the complex molecule to the oxidant or reductant through a 1,10-phenanthroline bridge. With a substance like hydroquinone, another possible mechanism involves displacement by a hydroquinone molecule of a 1,10-phenanthroline molecule as

$$FePh_n^{+++} + Ph \rightleftharpoons FePh_{n-1}^{+++} \quad (1)$$

$$FePh_n^{+++} + QH_2 \rightleftharpoons (Fe_{n-1}QH_2)^{+++} + Ph \quad (2)$$

and the hydroquinone complex may subsequently react to give the desired products. Equation 2 is written as an equilibrium displacement reaction because this provides a very plausible reason for the inverse order in 1,10-phenanthroline, and it fits in with the theory, substantiated in other reactions[2] in which such complexes are intermediates; the concentrations are, however, too low for the complex containing hydroquinone to be kinetically detectable. The integer, n, is probably two or three.[3] The kinetics for this mechanism would be expressed by the equation

$$\frac{-d[A]}{dt} = \left[\frac{k_1K_1K_2[QH_2]}{1 + K_1[Ph]}\right][A] \quad (3)$$

(1) Work was performed in part in the Ames Laboratory of the Atomic Energy Commission.

(2) F. R. Duke and R. F. Bremer, THIS JOURNAL, **73**, 5179 (1951) and the references in footnote 2, this reference.

(3) A. Gaines, Jr., L. P. Hammett and G. H. Walden, Jr., *ibid.*, **58**, 1668 (1936).