Removing Micronutrient Metal Cation Interferences Prior to Titrimetric Determination of Polyphosphate Chain Length

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Evaluation of chain lengths of polymeric phosphates is essential for the characterization of polyphosphate-based fertilizers. The titrimetric method, which is the most reliable and simple means of determining number average chain lengths ($\bar{n}$), cannot be applied to solutions containing micronutrient ions. In this investigation, methods have been proposed for the elimination of metal ion interference prior to the titrimetric determination of the average chain length of polyphosphate solutions. When Cu^{2+}, Fe^{3+}, Mn^{2+}, Mg^{2+}, or Mo^{6+} are present in the solutions, solvent extraction of their complexes with 8-hydroxyquinoline at appropriate pH, prior to titration, was very effective. The interference due to Zn^{2+} was conveniently masked by the addition of potassium ferrocyanide and the titration carried out in the presence of the insoluble complexes. These methods do not introduce any perceptible additional error in the determination of $\bar{n}$. They can also be conveniently combined when more than one interfering ion is present in the polyphosphate solution. These methods, therefore, offer a rapid, simple, and reliable means for analyzing micronutrient polyphosphate fertilizers.

Keywords: *Polyphosphate titration; chain length; analysis; interference; metal ions*

INTRODUCTION

Various polymeric compounds of phosphates ranging from the low molecular weight pyrophosphates to the very high molecular weight metaphosphates and glasses have been suggested for use as fertilizers. Thus, condensed phosphoric acid is often treated with selected micronutrient cations to function both as phosphate and micronutrient sources (Mortvedt and Cox, 1985). Crystalline metaphosphates such as potassium metaphosphate and phosphate glass frits may similarly be enriched with Mg^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, etc. (Sauchelli, 1969; Silverberg et al., 1972; Volfkovich, 1972; Wilson, 1988). Smaller chain polyphosphates have also been introduced as slow release micronutrient sources (Ray et al., 1993, 1997). For the characterization and study of any polymeric phosphate fertilizer, the determination of chain length is an important aspect.

The various techniques currently in use for the analysis of polyphosphates include titrimetry (Van Wazer, 1966); paper chromatography and ion-exchange chromatography (Ramsay, 1986); XRD and NMR (Rieman and Beukenkamp, 1961); and liquid chromatography coupled with plasma emission, etc. (Biggs et al., 1984). Of these, chromatographic methods are the most popular but are limited by the fact that individual species of the longer chain polymers cannot be determined, and therefore, the average chain length cannot always be estimated. Biggs et al. (1984) reported that liquid chromatographic separation of polyphosphates coupled with a direct current plasma-atomic emission spectrometer could detect polyphosphates ranging from P_1 to P_{12}. Similarly, Nishimura et al. (1990) developed an ion-exchange chromatographic method for separation of condensed phosphates as they observed that condensed phosphates having a low degree of polymerization could be determined accurately. Methods such as these using ion exchange/chromatographic separations, however, often require neutralized samples which yield precipitates in the presence of various micronutrient cations, which thus requires the removal of the cations in order for the method to work properly. The various chromatographic separation techniques and their limitations are discussed in a review by Ramsey (1986). Gel electrophoresis was applied by Clark and Wood (1987) for the fractionation of biologically important long chain polyphosphates. Linders et al. (1985) developed a hybrid electrode for the determination of phosphates.

All the aforesaid methods can give quantitative estimates of individual polyphosphates, within a limited size range; none of them provide a direct estimate of the average chain length, $\bar{n}$ (Van Wazer, 1966). For the evaluation of $\bar{n}$ from such techniques, the whole range of polyphosphate species present has to be determined, which is often not possible. Only the titrimetric method is best suited for the analysis of polyphosphate mixtures having wide-ranging molecular weights, since it directly provides the value of the average chain length, $\bar{n}$. However, one major drawback of the titrimetric processes which seriously limits its applicability is the interference caused by metal ions. All such ions are interferents, which either consume alkali in the pH range 4−9 or precipitate as phosphate. Micronutrient-containing polyphosphates, therefore, cannot be analyzed by titration. To adapt the titrimetric technique for such systems, it is necessary to remove the interfer-

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Table 1. Removal of Cation Interference in the Titrimetric Analysis of Polyphosphates

interferant	method of removal	reagent	pH during extraction (workable range)	remarks	chain length of phosphate ($\bar{n}$)	
					pure solution	after removal of interferant
Cu^{2+}	solvent extraction	oxine in chloroform-isoamyl alcohol	8.0 (5.3−14.0)	titration performed after solvent extraction	8.6	8.6
Fe^{3+}			8.0 (2.0−10.0)		8.6	8.6
Mn^{2+}			8.0 (5.9−10.0)		8.6	8.6
Mg^{2+}			11.8		6.6	6.6
Mo^{6+}			5.6		6.6	6.6
Zn^{2+}	precipitation	potassium ferrocyanide		direct titration after addition of reagent	6.6	6.6
Cu^{2+}, Fe^{3+}, Mn^{2+}, Mg^{2+}, Mo^{6+}, Zn^{2+}	solvent extraction and precipitation	oxine in chloroform-amyl alcohol and potassium ferrocyanide	11.5, 8.0, 5.6	titration after solvent extraction and addition of reagent	6.6	6.6

ing ions from the solution prior to titration; such methods are, however, not yet available.

The objective of this study was the development of methods for removal of metal ions from polyphosphate solutions to enable the titrimetric determination of their average chain length. The methods should doubly ensure that foreign compounds are not introduced which may themselves be interfering and at the same time avoid drastic measures such as heating or strongly acidic conditions which cause rapid depolymerization of the polyphosphate chains. Here, studies have been done to develop methods for removal of some common micronutrient ions present in polyphosphate-based fertilizers, viz., Cu^{2+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, Mo^{6+}, and Zn^{2+}. Individual processes have been described for the removal of each of these ions. Where more than one ion is present, the respective processes may be readily combined.

MATERIALS AND METHODS

To standardize the methods for removal of ion interference, initially, all studies were carried out using orthophosphoric acid to which the interferant ions were added. The advantage of standardizing with the ortho acid is that there is no phosphate hydrolysis error due to change in the $\bar{n}$ which is always 1.0. Essentially, the process consists of adding a metal ion solution to a known amount of phosphoric acid, removing the metal ion from the phosphate solution by different means and then determining the chain length of the phosphate by the titrimetric method (Van Wazer et al., 1954). If the value, thus obtained, corresponds to 1.0, then the method is acceptable.

Subsequently, these methods for ion interference removal are applied to polyphosphoric acid, which was prepared by heating orthophosphoric acid (analytical grade) in a platinum crucible at 300 °C (Varadachari, 1992) for 30 min and then diluting with water to obtain a solution containing 185 mg of P/mL. The polyphosphoric acid had an average chain length ($\bar{n}$) of 8.6 (due to gradual hydrolysis of this solution on keeping, the $\bar{n}$ was reduced to 6.6 in the course of the investigations). The polyphosphoric acid was mixed with various metal ions, and the solution was treated for interference removal and was then titrated as usual. The titration curves were assessed for the presence of the interferants; if a method was successful, the same titer values were obtained as for the pure polyphosphoric acid solution. All reagents used throughout the study were of analytical grade.

The titrimetric procedure for analysis of number average chain lengths of polyphosphate solutions free from interferants was developed by Van Wazer et al. (1954). The same procedure, which has been used here, is described as follows.

Titration 1. The sample solution containing about 2 mg of P was taken in a beaker and if necessary, 0.1 N HCl was added to lower its pH to around 3.0. The solution was then titrated pH-metrically beyond its end point near pH 9.5, using standardized 0.1 N NaOH. The amount of base required to titrate from the first end point (around pH 4.5) to the second end point (around pH 9.5) equals the total weakly acidic functions (end group P).

Titration 2. To the same sample, after completion of the titration 1, 0.1 N HCl was added to lower its pH to around 3 and then titration was continued to just beyond the first end point (at pH 4.5; excess base added, beyond the first end point at pH 4.5 should be considered in the final titer value). The titration was stopped momentarily, and sufficient (2 mL) 1 N $AgNO_3$ solution was added to precipitate orthophosphate as the Ag^+ salt. Titration was then continued beyond the moderately strong end point at around pH 5. The final titer value is the amount of base consumed from the end point at pH 4.5 to that around pH 5. This equals the total weakly acidic functional groups that are directly titratable plus the weakly acidic functional groups of orthophosphate that cannot be titrated directly. Thus, the amount of orthophosphate can be obtained from the amount of base consumed in titration 2 minus the base consumed in titration 1.

For the determination of total P in the sample, it was first hydrolyzed by heating an aliquot containing 0.1 N HCl at 90 °C for 200 h (a shorter period of heating results in incomplete hydrolysis, as observed in trial experiments). Alternatively, the sample may be fused with NaOH in a nickel crucible and neutralized with HCl. The solution was made up to volume and the P analyzed by titration 1.

In the absence of ring compounds, the value of number average number of P atoms per chain ($\bar{n}$) is evaluated as $\bar{n}$ = [{2 (total P − orthophosphate P)}/{end group P − orthophosphate P}]. This value of $\bar{n}$ excludes the orthophosphate. If the ortho group is to be included in the value, then $\bar{n}'$ (including ortho) = $[\bar{n}/o(n - 1) + 1]$ (Van Wazer, 1966), where o = weight fration of total P as orthophosphate.

Methods for the Removal of Cation Interference. The following methods were developed for the removal of interfering metal ions from polyphosphate solutions after numerous trials with various solvent extraction and precipitation techniques (Bassett et al., 1986; Cooper, 1961; Kanzelmeyer, 1961; Sandell, 1959; Snell and Snell, 1959).

Copper. A copper(II) phosphate solution was prepared by mixing $CuSO_4 \cdot 5H_2O$ with ortho or polyphosphoric acid in the weight ratio Cu:P = 1:7.5. An aliquot containing about 7.5 mg of P and 1.0 mg of Cu was taken in a dry separating funnel and its pH adjusted to 8.0 (or anywhere within 5.3−14.0) by addition of a known amount of 0.1 N NaOH. In this pH range, the extraction of the Cu^{2+} complex is known to be complete (Snell and Snell, 1959). In fact, all the extractions detailed here for metal−oxinate complexes have been done at the optimum pH range which will result in complete quantitative removal into the solvent layer. The volume was made up to 20 mL with the requisite amount of water. Then a 0.1% solution of oxine (8-hydroxyquinoline) in a chloroform-amyl

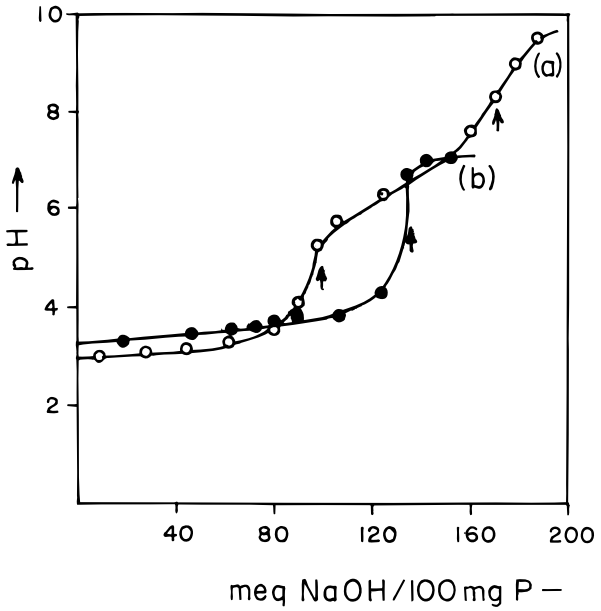

Figure 1. Titration curves of polyphosphoric acid; (a) titration 1; (b) titration 2.

alcohol (6:1, v:v) mixture was added. Every 1.0 mg of Cu^{2+}, in a solution volume of 20 mL, required three extractions each with 10 mL of the oxine solution. For solutions containing larger amounts of Cu^{2+}, further extractions were necessary. The separating funnel was throughly shaken, and the solvent layer was drained out after allowing time for settling (about 30 min). Complete extraction may be visually judged by absence of the color (yellow) of the complex in the solvent layer. Subsequently,the solution was extracted once with chloroform-amyl alcohol mixture and twice with chloroform alone to remove traces of oxine. An aliquot of the Cu-free phosphate solution was then used for titrimetric analysis by the method described earlier.

Iron. To a solution of ortho or polyphosphoric acid, was added $(NH_4)Fe(SO_4)_2 \cdot 12H_2O$ to obtain a (Fe:P) weight ratio of 1:7.5. An aliquot was taken in a separating funnel and a predetermined amount of 0.1 N NaOH was added to raise the pH of the solution to 8.0 (or anywhere within 2−10); the solution volume was made up to 20 mL. A 0.1% solution of oxine was prepared as described earlier and the iron phosphate solution was repeatedly extracted with it. Extraction was continued about seven times until the color (black) of the iron complex was no longer present. (Every 0.2 mg of Fe required three extractions with the oxine solution.) The aqueous layer was finally washed with chloroform-amyl alcohol and chloro-

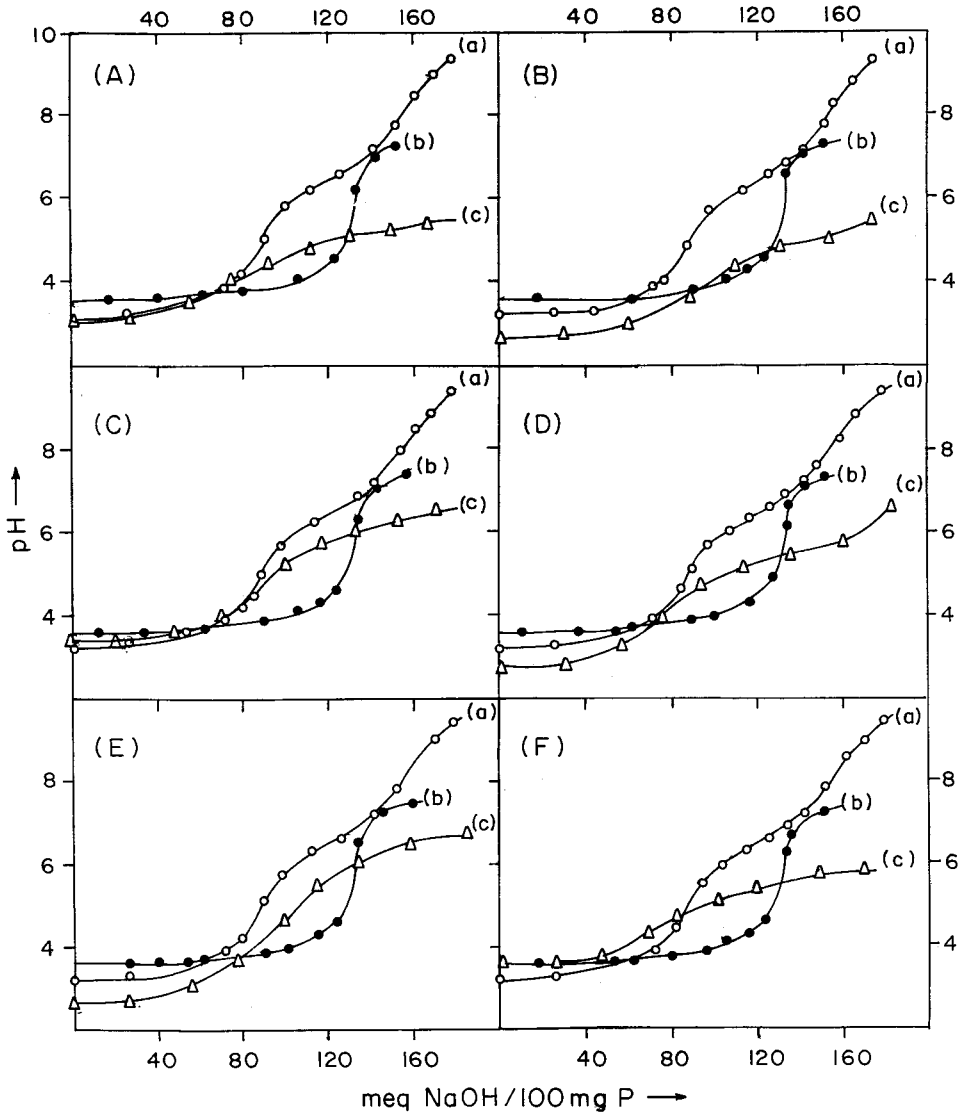

Figure 2. Titration curves of metal−polyphosphoric acid system: (a) after removal of metal ion with oxine (titration 1); (b) after removal of metal ion with oxine (titration 2); (c) in the presence of metal ion [A; Cu^{2+}; B, Fe^{3+}; C, Mn^{2+}; D, Mg^{2+}; E, Mo^{6+}; F, Zn^{2+}].

form to remove all traces of oxine. An aliquot of the Fe-free phosphate solution was then taken for chain length analysis.

Manganese. A solution of ortho and polyphosphate was prepared by adding $MnSO_4 \cdot 2H_2O$ to the respective acids such that the weight ratio Mn:P = 1:7.5. This was extracted as before, after adjusting the solution pH to 8.0 (or anywhere within 5.9−10.0). Five extractions were necessary for each milligram of Mn^{2+} in solution. The aqueous layer was washed free of oxine and subsequently taken for titration.

Magnesium. Magnesium ion was also extractable as the oxine complex although with some difficulty. An aliquot of the solution (containing ortho or polyphosphate and Mg^{2+} as $MgSO_4 \cdot 7H_2O$, weight ratio Mg:P = 1:7.5) at pH 11.5 was extracted as described earlier. For 1 mg of Mg^{2+}, seven extractions with oxine solution (10 mL each time) were required. During the extraction, excessive shaking of the funnel had to be avoided since magnesium oxinate readily hydrates and becomes insoluble in the organic phase. Following extraction with pure solvent, the aqueous layer was taken for titration.

Molybdenum. The phosphate solution containing Mo^{6+} [as $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] was extracted at pH 5.6 with oxine solution as before. With each addition of the oxine solution, the separating funnel was thoroughly shaken for 10 min. If the period of shaking was decreased, the complex was incompletely extracted. Nine such extractions were required for every 0.5 mg of Mo^{6+}. This was subsequently washed as usual, with pure solvents and then taken for chain length analysis.

Zinc. Zinc cannot be extracted as the oxinate complex. However, interference due to the Zn^{2+} ion may be readily eliminated by complexation with ferrocyanide. An aliquot of the solution to be titrated, containing Zn^{2+} (Zn metal, dissolved in HCl) and ortho or polyphosphoric acid (Zn:P = 1:7.5, weight ratio), was taken in a beaker, and to it, excess of $K_4[Fe(CN)_6]$ (four times the weight of Zn^{2+}) was added. The solution was stirred and titrated as usual. Unreacted $K_4[Fe(CN)_6]$ that was present in the solution did not interfere with the titration. However, during the $AgNO_3$ titration, care was taken so that the amount of $AgNO_3$ was sufficient to compensate for the Ag^+ that was precipitated as the ferrocyanide salt.

Copper, Iron, Manganese, Magnesium, Molybdenum, Zinc. In a polyphosphate solution containing one or more of the interferants, the methods for their removal may be combined. The procedure adopted for the removal of interference from an ortho or polyphosphate solution containing all six aforementioned ions was as follows. To an ortho or polyphosphoric acid solution, Cu^2 , Fe^{3+}, Mn^{2+}, Mg^{2+} , Mo^{6+}, and Zn^{2+} were added in equal amounts so that the net weight ratio M:P = 1:7.5. To this solution, in a separating funnel, a pre-estimated quantity of 0.1 N NaOH was added to raise its pH to 11.5 and the procedure described for removal of Mg^{2+} was followed. Subsequently, the pH of the solution was reduced to 8.0 by adding a known amount of 0.1 N HCl and extraction with oxine solution was repeated once again to remove Cu^{2+}, Fe^{2+}, and Mn^{2+}. Finally, the solution pH was lowered to 5.6 with further addition of a predetermined amount of 0.1 N HCl (3.9 mL) and extraction with oxine solution was done as described for Mo^{6+}. An aliquot of the solution was taken in a beaker, its pH was lowered to around 3.0 and $K_4[Fe(CN)_6]$ was added in excess to precipitate Zn^{2+}. This solution was titrated for chain length analysis by the usual procedure.

Along with each titration carried out after treatment for removal of interferant, titration of the pure polyphosphoric acid solution was also done. Thus, the average chain lengths obtained for the two (pure and treated) solutions were compared only in titrations carried out on the same day.

RESULTS AND DISCUSSION

A summary of the methods for the removal of metal ion interference in polyphosphate titration is given in Table 1. Figure 1 shows the titration curves for pure polyphosphoric acid. Titration curves in the presence of interferants and after removal of the interferants are reported in Figure 2. The difference between the first and second inflections (end points) in the polyphosphate titration (Figure 1, curve a; titration 1) is a measure of the weakly acid end group P. Also, in the presence of interferants, the first and/or second inflections change in position and even may not be obtained due to consumption of alkali by the cations (Figure 2, curve c in all panels). This may, however, be noted that the nature of the titration curve of polyphosphate in the presence of interfering cation varies with the amount of the cation; buffering zones become larger, end points are less distinct and alkali consumption is higher when larger amounts of interferants are present. However, after the removal of interferants, titration curves (Figure 2, curves a and b in all panels) are identical to those of polyphosphoric acid (Figure 1, curves a and b). Thus, cation interference is completely suppressed (Figure 2) and the solution can be titrated as usual.

The treatments for the removal of interferants introduced no extra error; the error (±0.2%) is within the range of error inherent in the titrimetric method itself. Thus, the $\bar{n}$ value obtained for polyphosphoric acid solutions containing metal polyphosphates is the same as in pure polyphosphoric acid (8.6 or 6.6).

The methods recommended in Table 1 were selected after careful analysis of numerous trials. Thus, when Cu^{2+} was complexed with $K_4[Fe(CN)_6]$, as was done with the Zn^{2+} ion, the titration was unsuccessful since $Cu_2[Fe(CN)_6]$ readily dissociates forming the hydroxide. Interference from Cu^{2+} or Fe^{3+} could be removed by the addition of carbamate (sodium diethyldithiocarbamate); however, this method cannot be used since excess carbamate itself interferes in the titration. On the other hand, the oxinate extraction is very successful for the removal of all micronturient ions studied here except Zn^{2+}.

For polyphosphate solutions containing two or more of such metal ions, the individual methods for their removal may be combined. This is readily done since there are essentially only two methods, viz., solvent extraction with oxine and precipitation as ferrocyanide. Hence, in a solution of polyphosphate containing Cu^{2+}, Mn^{2+}, Fe^{3+}, Mg^{2+}, Mo^{6+} , and Zn^{2+}, solvent extraction with oxine using the chloroform-isoamyl alcohol mixture at the relevant pH and addition of ferrocyanide prior to titration can suppress all interference. If the solution contains Mg^{2+} ions, the oxine extraction for Mg^{2+} needs to be done first. This is necessary in order to avoid hydration of the magnesium oxinate, which makes it insoluble in the organic phase. The pH of the solution is then sequentially lowered to extract the other metal oxinates which may be present. For any combination of ions in the solution, the maximum number of treatments necessary consists of only three solvent extractions and the addition of complexant. Average chain lengths of solution metal polyphosphates can, therefore, be determined rapidly, accurately and quite simply.

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