Comparison of polyphosphate analysis by ion chromatography and by modified end-group titration

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Abstract

The need to characterize polyphosphates by the number of phosphorus atoms in the polymer chain has been an increasing interest in the phosphate manufacturing and food-processing industries. Various modifications of end-group titration are probably the most widely accepted methods of characterizing polyphosphates. Ion chromatography (IC) offers a new analytical approach in depicting the average chain length ($\bar{n}$) and a profile of the product being analyzed. Commercially available microbore IC columns provide baseline separation of cyclic and linear polyphosphates in the first portion of the chromatogram. Several sodium hexametaphosphate (SHMP) samples with a wide range of chain lengths, as determined by titration methods, were used for this comparison study.

Keywords: Polyphosphates

1. Introduction

Condensed phosphates is a generic term for all phosphate polymers, either linear or cyclic, resulting from the elimination of water between orthophosphoric acid molecules or orthophosphate salts. During their manufacture as the acid or salt, control of the final mixture is both an art and a science. Under certain conditions, when phosphoric acid and soda ash are blended in varying ratios and heated, relatively reproducible mixtures are manufactured for various applications, including use in foods. Fig. 1 illustrates various pathways to some of these products, none of which is a pure component but a mixture of varying degrees of polyphosphates [1–4].

Numerous procedures have been developed to characterize these mixtures to estimate the average

chain length ($\bar{n}$). Two of these modified titration procedures are discussed here [2,5]. This paper also describes the use of a 2 mm I.D. microbore ion chromatographic system with the Dionex IonPac® AS11 column. This column, used with a NaOH gradient has expanded our ability to characterize polyphosphates with improved peak resolution over the Dionex PAX-100 column used with NaOH
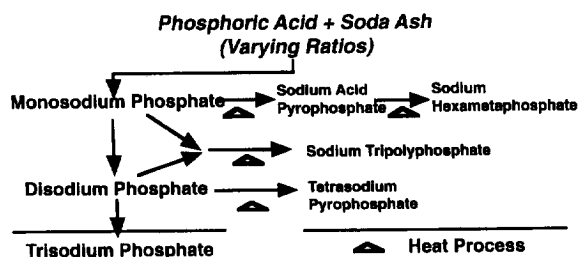

Fig. 1. Relationships of orthophosphates and polyphosphates in their commercial production.

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gradient [6–8]. Individual polymer standards, however, are not available above four phosphorus units for quantification. Only estimates based upon peak area and ratios between peaks are presently available. In addition to bulk phosphate production samples, seven 1-g samples with certified average chain lengths ($\bar{n}$) of 5 to over 75 are commercially available.

2. Experimental conditions

2.1. Ion chromatography method

2.1.1. IC instrument

The basic instrument was a Dionex 4500i (Sunnyvale, CA, USA) microbore system with an advanced gradient pump, a 20 μl sample loop and a Pulsed Electrochemical/Conductivity detector. The Anion Self-Regenerating Suppressor was operated in the auto-suppression recycle mode. The data acquisition and instrument control was performed using a Dionex AI-450 v. 3.32 program on a Compaq 4/66 computer with a Hewlett-Packard Laser Jet IIIp printer.

2.1.2. IC columns

The 2×50 mm guard and 2×250 mm analytical columns used in this work were the Dionex IonPac® AG11 and IonPac® AS11, respectively. A Dionex anion trap column (ATC, 2 mm) was placed between the eluent pump and the injection valve.

2.1.3. IC reagents and standard solutions

Deionized distilled water with a specific resistance of $\geq$18 MΩ (DI water) from a Millipore (Bedford, MA, USA) Milli-Q Plus PF water purification system. This DI water was used to prepare all reagents and standards. DI water for eluents was sparged with helium before solutions were made and sparging continued for the life of the eluent mixture.

Sodium hydroxide 200 mM eluent was prepared by dilution from the certified grade, carbonate-free 50% (w/w) NaOH solution (Fisher, Pittsburgh, PA, USA). Using a clear, disposable pipette, 16.00 g (10.50 ml) of 50% (w/w) was quickly transferred into 984 g of degassed DI water.

Sodium phosphate glasses (SPG), also called

SHMP, of various chain lengths (Type 5–Type 75) from Sigma (St. Louis, MO, USA) were used as controls for both the IC and titration methods.

All IC reagents used for standards were of the highest available purity and were purchased as follows: PO$_4$ as monobasic potassium phosphate (KH$_2$PO$_4$) Aldrich, (Milwaukee, WI, USA), P$_2$O$_7$ as sodium pyrophosphate (Na$_4$P$_2$O$_7$) Aldrich 98%, P$_3$O$_9$ as trisodium trimetaphosphate (Na$_3$P$_3$O$_9$) Grade III Sigma 98%, P$_3$O$_{10}$ as tripolyphosphate pentasodium salt hexahydrate (Na$_5$P$_3$O$_{10}$·6H$_2$O) Sigma, P$_4$O$_{13}$ as tetrapolyphosphate hexammonium salt ((NH$_4$)$_6$P$_4$O$_{13}$) Sigma.

A working solution containing all of the five components (PO$_4$, P$_2$O$_7$, P$_3$O$_9$, P$_3$O$_{10}$ and P$_4$O$_{13}$) was made from a 1:10 dilution of each of the separately prepared 1000 ppm stock standard solutions. The purity of the individual stock standards was determined by serial dilution and calculation of the contribution of the minor components. Solutions were not used for more than one day.

2.1.4. IC sample preparation

The samples were diluted on a w/w basis using DI water, to allow each component to be within the calibrated range. For SHMP or SPG, a final working solution of approximately 150 μg/g was used for the assay condition presented in this study. Where possible, an appropriate dilution was made to obtain data for all five components (if present) in a single run. All solutions were filtered through a 0.2 μm Anotop IC membrane (Whatman, Fairfield, NJ, USA) prior to sample injection.

2.1.5. IC operating procedure

The 60 min gradient program was increased from 20 mM NaOH to 140 mM NaOH over the initial 47 min period at a constant flow-rate of 0.3 ml/min.

Eluent E1=200 mM NaOH.

Eluent E2=degassed Type 1 deionized water.

Time (min)	%E1	%E2
0.0	10	90
0.1	10	90
40.0	70	30
47.0	70	30
48.0	10	90
60.0	10	90

2.2. Titration methods

2.2.1. Titration instrumentation

All titrations were performed using a Brinkmann 702 SM Titrino (Westbury, NY, USA) equipped with a programmable 702 keyboard, 703 Ti Stand and DPU-411 Type II thermal printer.

2.2.2. Titration reagents

Dilute hydrochloric acid solution (3 M) was prepared from analytical-reagent grade concentrated hydrochloric acid. Sodium hydroxide solutions (3 and 0.1 M) were prepared from a 5 M NaOH solution (Fisher). The 0.1 M NaOH used for all titration procedures was standardized against dried high-purity-grade potassium biphthalate ($C_8H_5O_4K$) (Fisher). DI water was used throughout.

2.2.3. Titration procedure

Method A: Modified end-group titration with hydrolysis [5].

Method B: Modified end-group titration without hydrolysis [2].

The auto-titrator was programmed to print out the average chain length ($\bar{n}$) based upon fixed pH values of 4.50 and 9.50.

3. Results and discussion

The hydrolysis of condensed phosphates is of great practical interest because the ultimate breakdown product, orthophosphate, does not posses either the sequestering or dispersing properties of the larger parent molecule. It is, therefore, of utmost importance for an analyst to understand what may happen
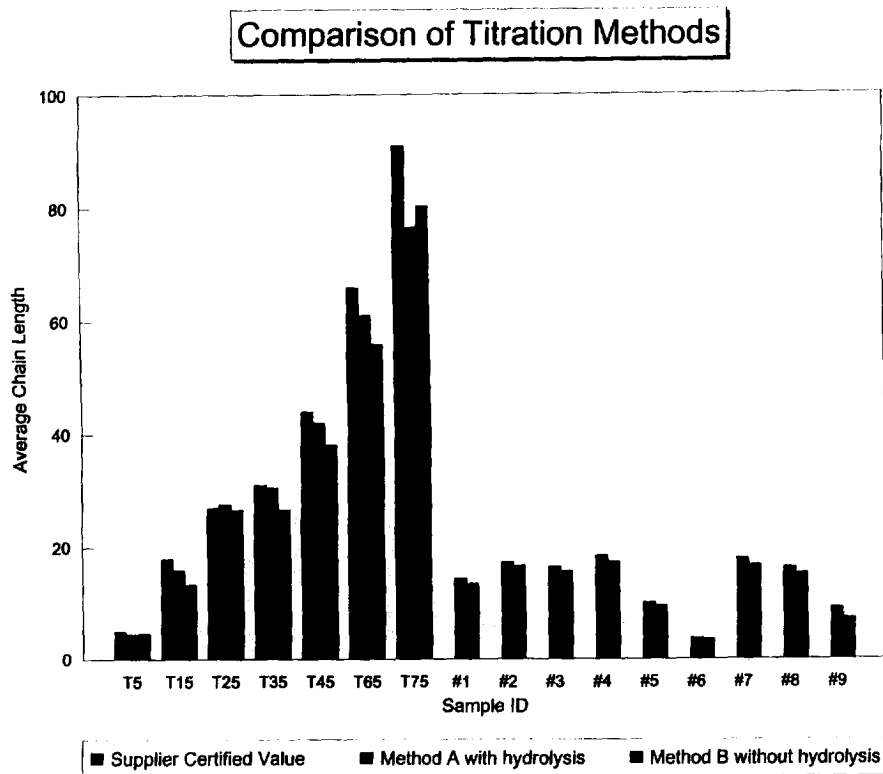

Fig. 2. Comparison of titration results of Method A and Method B shows a distinct bias. This gives reason to be cautious when using evaluation data from different end-group methods.

to a sample of a condensed phosphate when it is taken into solution. It has previously been reported that a relationship exists between the sequestering power of condensed phosphates and its average chain length ($\bar{n}$) [1].

Although the titration methods presented in this paper are time-consuming, especially with a hydrolysis step involved, they are, however, useful analytical tools for many quality control needs in industry. Both of these methods provide a number that can be used to monitor a specific parameter during processing or in the finished product, as well as for shelf-life stability studies. Method B eliminates the hydrolysis step but it still provides a single average value as a result and it provides no information about the distribution of the individual components. Fig. 2 provides a comparison between the two titration methods with a distinct bias. Method A usually results in a higher value. Each data point shown is the average of two or more analysis with the spread of data points no greater than 0.2 ($\bar{n}$). If the hydrolysis step is performed without a reflux, as presented in this study, the results can be more variable because of the loss of some of the hydrolyzing acid. In addition, different results can also be obtained depending upon whether fixed pH values or titration inflection points are used for the calculation. Therefore, it is critical to be specific, as well as consistent on establishing parameters for a given titration application and in the discussion of results between laboratories.

The IC method provides more information about specific individual components and the ratio of the various condensed polyphosphates present. Thus a better understanding of the product is obtained. Fig. 3 depicts three of the seven available SPG reference samples (SPG Types 5, 15 and 35). As can be seen, the linear series and the cyclic series of polyphosphates are readily identified using standards for comparison, even though only a few of the lower members of each series are commercially available in sufficient purity for quantitative work. The linear P_2O_7, the cyclic P_3O_9 and the linear P_3O_{10} are easily separated with the AS11 column and standards are available for quantification. Their ratios can be used as an indirect measure of the average chain length. Qualitatively, the higher the ratio of cyclic to linear P_3, the higher the average chain length ($\bar{n}$) in an
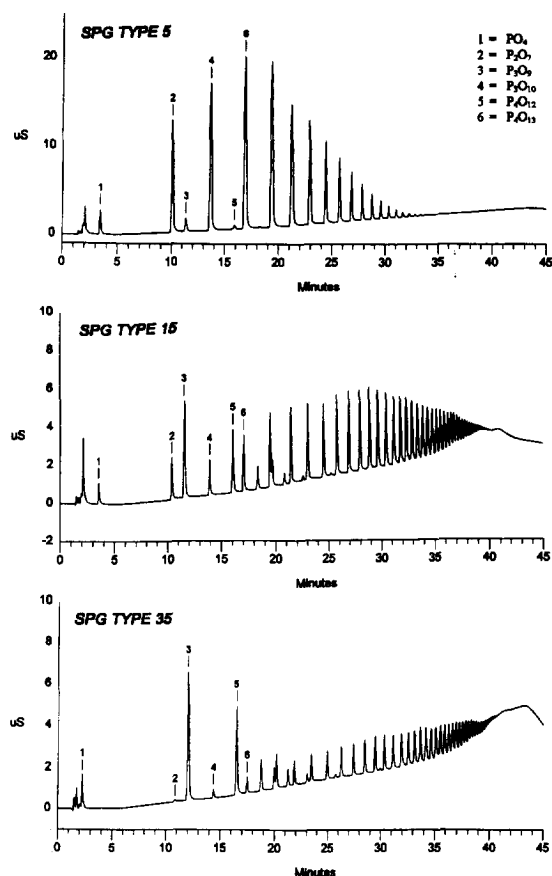

Fig. 3. IC profiles of three of seven commercially available standard sodium phosphate glass (SPG) from Sigma.

equilibrium mixture solution from one product (Fig. 3 and Fig. 4). If, however, the solution is the result of two or more dry product preparations mixed into the same solution, the ratios may not be consistent with the overall profile.

Any polyphosphate may be characterized by this IC method, but samples having an ($\bar{n}$) greater than 45 have only minor measurable differences other than the P_3 ratio. Under these chromatographic conditions, although both linear chains and cyclics are all in one injection, not all of the sample's higher fractions are eluted. However, by looking at the first 25–30 readily separable peaks, we can get a fingerprint that qualitatively describes the sample with specific information on its relative composition. The IC method can possibly follow storage changes that
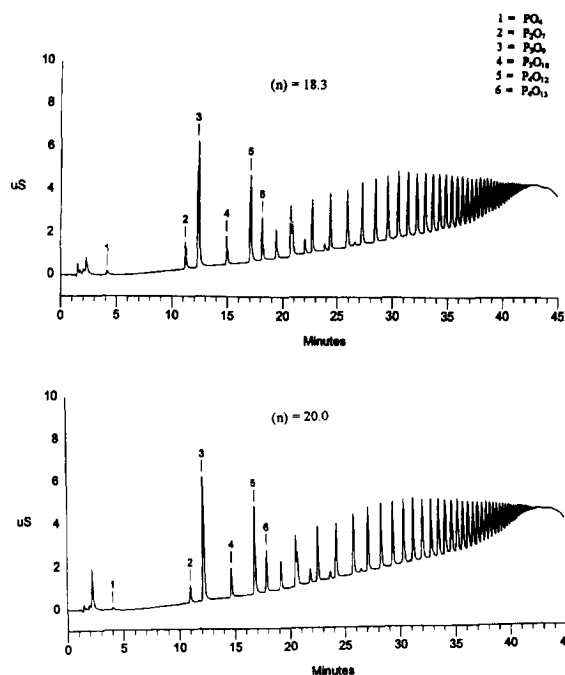
Fig. 4. IC profile examples of two similar commercial food-grade SHMP. The ratio of the cyclic to the linear P_3 is related to the average chain length $(\bar{n})$.
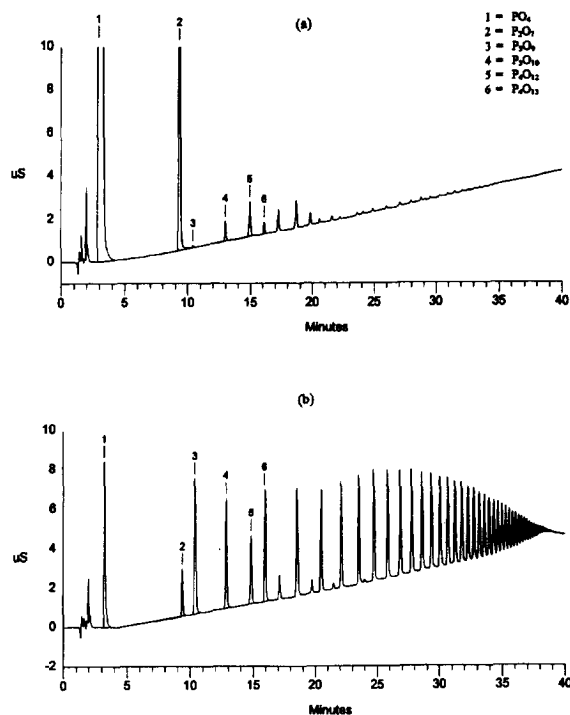

Fig. 5. IC profiles of two 50% solutions prepared from the same lot of SHMP powder; (a) 'bad' batch, (b) 'good' batch. A practical problem in solution preparation of SHMP was identified by IC.

occur from hydrolysis of metaphosphates such as those added to various products.

Fig. 5 demonstrates a practical situation where two 50% SHMP solutions were prepared from the same lot of dry powder but produced finished cheese product of quite different characteristics. The chromatographic profiles describe the degree of hydrolysis at a critical step in the plant operation. This information led to solving a solution-handling problem in the cheese plant.

The IC method can also reveal if the sample is composed of a mixture of two different polyphosphates of different composition having different functional characteristics. A foreign supplier provided a sample that was supposedly the same as sodium tripolyphosphate (STP), but it did not function in the same way as domestic STP (Fig. 6). The cause of the different functionality would not be detected by any titration or other end-group method because of the percentage of hexametaphosphate present. This difference in samples was further

evaluated by examination under the microscope, followed by sieving and analyzing the sieve fractions of the foreign sample by IC. In addition, the estimated average chain length of the hexametaphosphate could be evaluated by the amount of cyclic P_3 and P_4 relative to the higher linear components.

4. Conclusion

The average chain length $(\bar{n})$ obtained by two titration procedures differed with a distinct bias in results. They are, however, reproducible and useful for many quality control applications.

The 2 mm IC microbore technology approach to the analysis of polyphosphates offers more than just a single number, $(\bar{n})$, that end-group methods provide. The use of the AS11 column allows baseline or near-baseline separation of the lower members of the polymer series such that a study of cyclic-to-linear
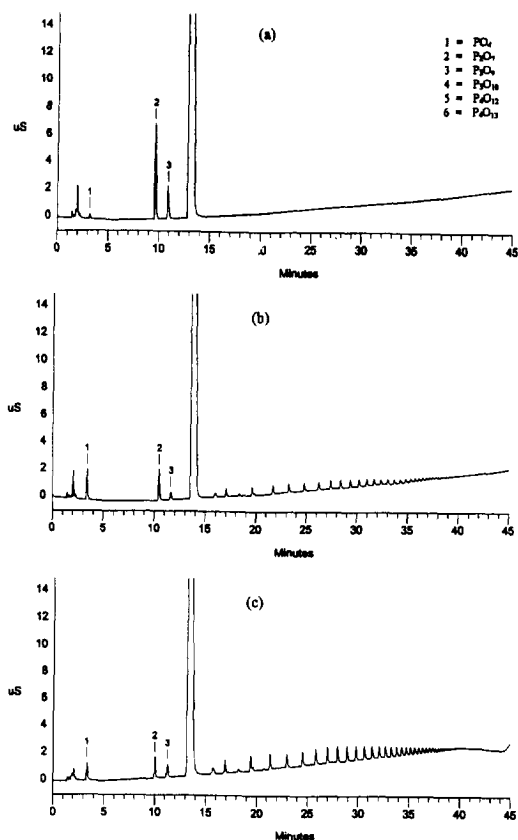
Fig. 6. (a) A domestic sample of STP; (b) A sample of a foreign-supplied sodium tripolyphosphate (STP); (c) A 200+ mesh sieve fraction of the foreign supplier's sample. The foreign supplier had added or contaminated STP with a small amount of SHMP. The functionality of the mixture was different from the 'pure' sample, (a). Most of the SHMP was found in the small mesh size. With cyclic-to-linear ratios, the character of the SHMP can be evaluated.

ratios can be conducted with useful data. Further, the chromatogram can yield a semi-quantitative finger-print of individual phosphate chain lengths up to about chain length thirty. The chromatograms clearly

show a fairly accurate means to determine lot-to-lot variation for SHMP production, and, potentially, they can be used to compare food application functionality with different SHMP compositions.

Acknowledgments

References

[1] S. Greenfield and M. Clift, Analytical Chemistry of Condensed Phosphates, 1st Edition, 1975.
[2] E.J. Griffith, J. Am. Chem. Soc., 79 (1957) 509–510.
[3] A.D.F. Toy, Comprehensive Inorganic Chemistry, Vol. 2, Chapter 20, J.W. Arrowsmith, Bristol, 1973.
[4] A.D.F. Toy and E.N. Walsh, Phosphorus Chemistry in Everyday Living, 2nd Edition, American Chemical Society, Washington, DC, 1987.
[5] J.R. VanWazer, E.J. Griffith and J.F. McCullough, Anal. Chem., 26 (1954) 1755–1759.
[6] Application Note AN71, Dionex, Sunnyvale, CA, August 1991.
[7] E.S. Baluyot and C.G. Hartford, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 1995, Abstract 258.
[8] F.S. Stover, J.A. Bulmahn and J.K. Gard, J. Chromatogr. A, 688 (1994) 89–95