Determination of Polyphosphates Using Ion Chromatography with Suppressed Conductivity Detection

INTRODUCTION

Polyphosphates are used for a wide variety of industrial applications due to their sequestering and dispersing properties. Polyphosphate samples are commonly characterized by various end-group titration methods that provide an estimate of average polyphosphate chain length, but no information on the relative amounts of individual polyphosphate oligomers. Manufacturers and end-users of polyphosphates need to determine the distribution of polyphosphate chain lengths because chain length is known to affect sequestering and dispersing properties.[1–2] A rapid method for the separation of polyphosphates with chain lengths to about 35 phosphate units is presented in this Application Note.

In this method, polyphosphates are eluted from a 2-mm IonPac®AS11 anion-exchange column with a sodium hydroxide gradient. The ASRS® (Anion Self-Regenerating Suppressor®) is used to suppress the high hydroxide concentrations needed to elute large, multiply-charged polyphosphates. Steep hydroxide gradients can be used without a substantial increase in background conductivity because of the exceptional suppression capacity of the ASRS. As a result, suppressed conductivity detection can be used to directly generate polyphosphate chain-length distribution profiles. Popular applications of this method include:

- Rapid polyphosphate fingerprinting to determine batch-to-batch chain-length variations.
- Studies to compare polyphosphate function to chain-length distribution.
- Monitoring of polyphosphate degradation in solution or during storage.
- Quantification of short-chain polyphosphates in water treatment streams.

EQUIPMENT

Dionex DX-500 system consisting of:
- GP40 Gradient Pump, high-performance microbore configuration
- ED40 Electrochemical Detector or CD20 Conductivity Detector
- DS3 Conductivity Cell
- LC20 Chromatography Enclosure
- EO1 Eluent Organizer

PeakNet Chromatography Workstation

REAGENTS

Sodium hydroxide, 50% (w/w) (Fisher Scientific)
Deionized water, 18 MΩ-cm
Sodium phosphate dibasic, ACS reagent, 98% (Aldrich)
Tetrasodium pyrophosphate decahydrate, 99.5% (Fluka)
Hexammonium tetrapolyphosphate, 95% (Sigma)
Sodium tripolyphosphate, technical grade, 85% (Aldrich)
Trisodium trimetaphosphate, grade III, 98% (Sigma)

REAGENT PREPARATION

200 mM Sodium Hydroxide

Degas 990 mL of deionized water by sonicating while under vacuum for approximately 15 minutes. Add 10.3 mL of 50% sodium hydroxide solution, mix, and degas briefly. Pressurize to 5–10 psi with helium.

CONDITIONS

Column:	IonPac AS11 Analytical (2 x 250 mm) IonPac AG11 Guard (2 x 50 mm)
Trap:	2-mm ATC
Eluent:	Sodium hydroxide gradient (see figures for specific conditions)
Flow Rate:	0.25 mL/min
Inj. Vol.:	10 µL
Suppressor:	ASRS, recycle or external water mode

DISCUSSION AND RESULTS

"Fingerprinting" of complex mixtures such as polyphosphoric acid can be readily accomplished using 2-mm AS11 technology with a sodium hydroxide gradient. The AS11 column contains a hydroxide-selective resin, meaning that highly retained analytes can be eluted with lower hydroxide concentrations than previously possible using traditional anion-exchange columns. A maximum of 200 mM sodium hydroxide can be suppressed when using a 2 mm ASRS at a flow rate of 0.25 mL/min with a current setting of 125 mA. This method is also applicable to standard bore chromatography with the 4 mm AS11 for up to 200 mM sodium hydroxide at 1 mL/min when using a 4 mm ASRS with a current setting of 495 mA. For maximum eluting power, the 2-mm format is best. In Figure 1, more than 60 peaks in the polyphosphoric acid chromatogram are shown using a 2-mm system.

To perform this analysis, a convex gradient was used to elute the lower molecular weight polyphosphates more quickly, while simultaneously preserving resolution of the higher molecular weight, later-eluting peaks.

Figure 2 demonstrates one way this method is useful to the food industry. Relatively minor variations in polyphosphate chain-length distribution often can significantly alter a preservative's efficacy. In this example, taken from a recently published work by Elizabeth Baluyot and Clark

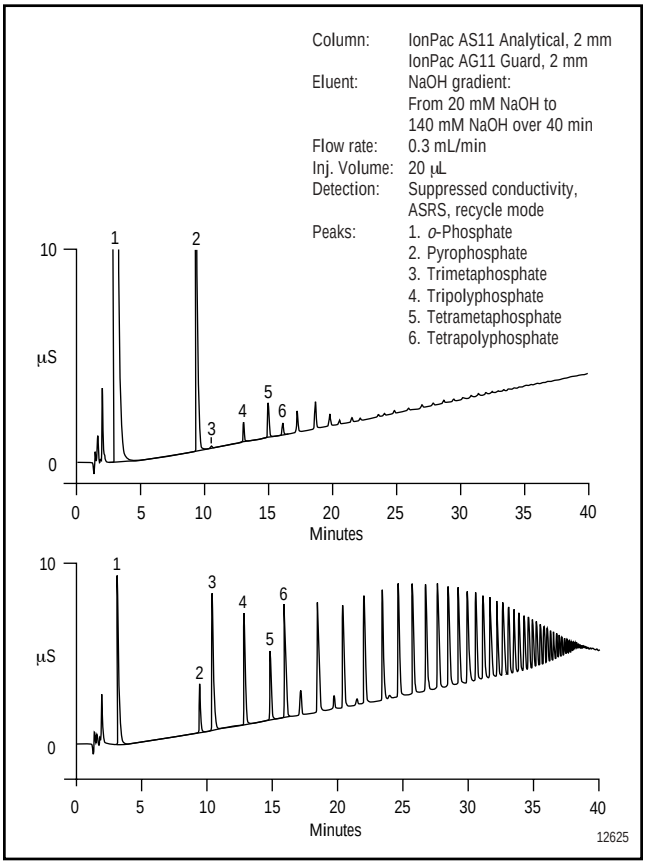

Figure 2 *Two lots of SHMP solution compared by ion chromatography. (Reproduced with permission from reference 2.)*

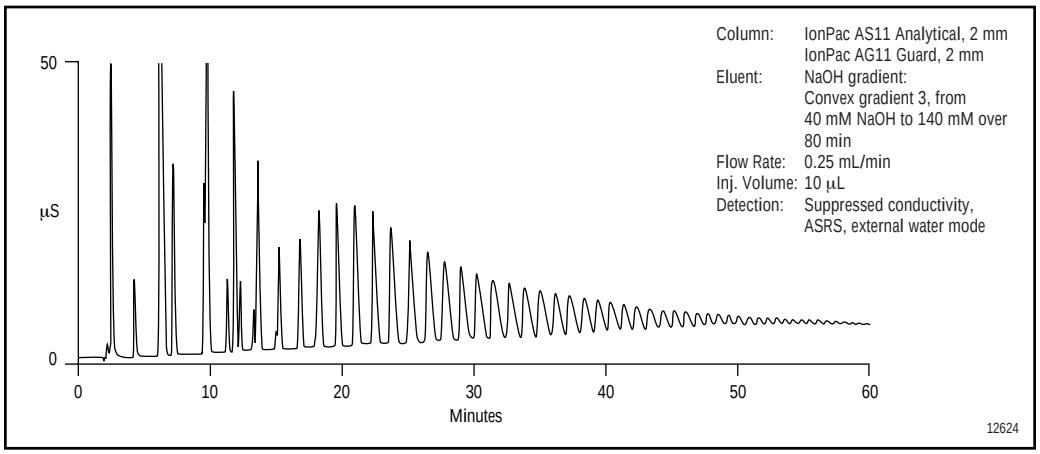

Figure 1 *Chromatogram of a 0.2% solution of polyphosphoric acid.*

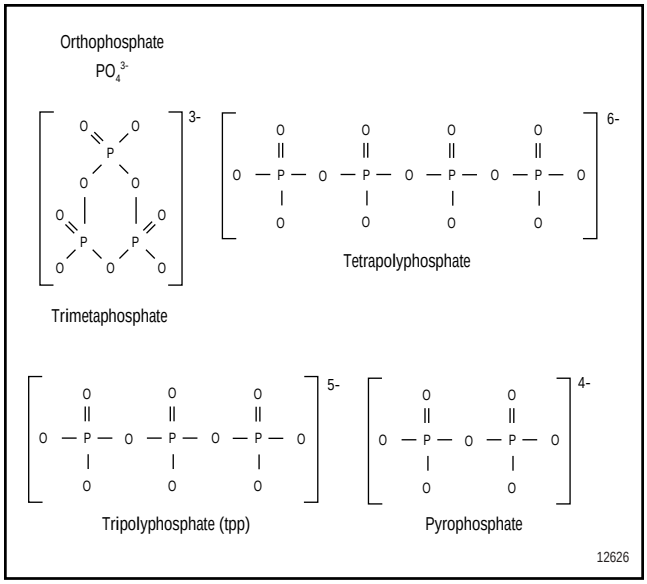

Figure 3 *Structures of commercially available phosphates suitable as standards.*

Hartford at Rhone-Poulenc[2], two batches of sodium hexametaphosphate (SHMP) solutions were fingerprinted. Although only slight batch-to-batch differences could be detected by titration, the chromatographic analysis revealed obvious differences in chain-length distributions. As a result, quality control for this product was improved.

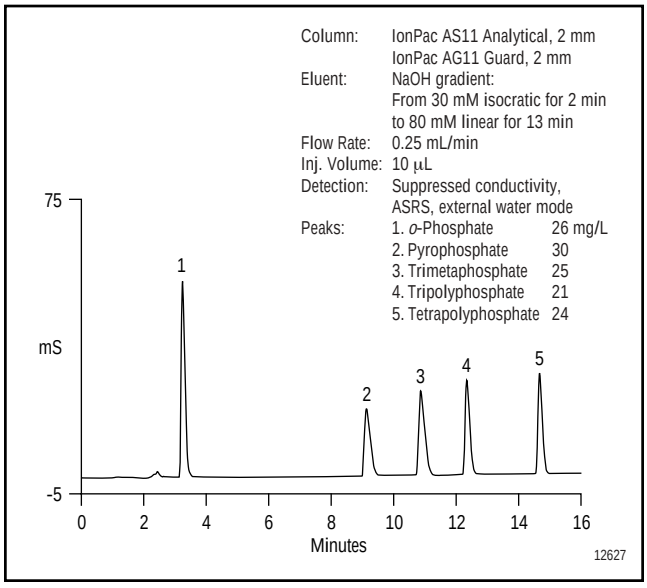

Figure 4 *Chromatogram of five standard phosphates.*

Method Performance

Pure, commercially available standards are available for only five condensed phosphates: *o*-phosphate, pyrophosphate, trimetaphosphate, tripolyphosphate, and tetrapolyphosphate. The structures of these phosphates are shown in Figure 3, and a chromatogram showing their elution order is seen in Figure 4. Method performance was evaluated for these commercially available standards.

Minimum Detectable Limits (MDL)

A volume of 10 µL of a standard containing 33, 38, 31, 26, and 30 µg/L of ortho-, pyro-, trimeta-, tripoly-, and tetrapolyphosphate, respectively, was injected. Detection limits, estimated at 3 times the background noise, were approximately 5, 30, 30, 20, and 20 µg/L.

Linearity

Linearity was investigated by serially diluting a stock solution containing 120, 110, and 120 mg/L of trimetaphosphate, tripolyphosphate, and tetrapolyphosphate, respectively. The resulting calibration standards were injected to determine linear ranges for these three species.

The *o*-phosphate stock solution contained 130 mg/L and was diluted serially and injected. Pyrophosphate calibration standards were similarly prepared from a stock solution of 80 mg/L. Linearity for *o*-phosphate and pyrophosphate was studied independently to avoid skewing the data with degradation products of the larger polyphosphates. Results for all species are listed in Table 1.

PRECAUTIONS

Sample Stability

Cyclic (also known as "meta") phosphates are more stable in aqueous solution than linear polyphosphates. High temperatures and low pH will accelerate hydrolysis, so keeping the samples cool will help preserve them. If necessary, the sample pH can be adjusted with sodium hydroxide to further slow degradation.

Another possible factor contributing to sample degradation is enzymatic activity. Phosphatases are found on the surface of human skin, so gloves should be worn to avoid sample contamination.

Table 1 Linear range for five commercially available phosphates	
o-Phosphate	2.5 to 130 mg/L[a] r^2 = 1.0000
Pyrophosphate	1.6 to 80 mg/L[a] r^2 = 0.9996
Trimetaphosphate	1.8 to 120 mg/L[b] r^2 = 1.0000
Tripolyphosphate	1.6 to 110 mg/L[b] r^2 = 0.9999
Tetrapolyphosphate	1.8 to 120 mg/L[b] r^2 = 0.9994
[a] Represents six data points, n=3 [b] Represents seven data points, n=3	

Gradient Chromatography

A 2-mm ATC trap column is required for use in gradient methods to trap anionic contaminants, such as carbonate, which may be present in the eluent. By placing the ATC between the pump and injection valve, baseline shifts and extraneous peaks during gradient analysis are minimized.

ASRS Modes

The work shown in this Application Note was done using the 2-mm ASRS in external water mode. This is the mode of choice when:

- Ultimate sensitivity is required.
- Exceptionally high sodium hydroxide concentrations are used (>200 mM).
- Organic solvent is present in the mobile phase.

For most polyphosphate analyses, the more convenient recycle mode is suitable.

REFERENCES

1. Greenfield, S.; Clift, M. *Analytical Chemistry of the Condensed Phosphates. 1st Edition*, **1975**.
2. Baluyot, E.S.; Hartford, C.G. *J. Chromatogr. A.* **1996**, *739*, 217–222.

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