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Determination of polyphosphates in intermediate materials for detergent manufacture by ion high-performance liquid chromatography with post-column derivatization

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ABSTRACT

A method for the determination of polyphosphates [ortho- (P_1), pyro- (P_2), tripoly- (P_3), and trimeta- (P_4) phosphate] based on the use of ion chromatography and gradient elution is proposed. The method was optimized for application to intermediate products in detergent manufacture, which feature rather different concentrations of the analytes (90–95% P_3 and 10–5% for the sum of the other three). The proposed method was applied to real samples with good results and throughput of four samples per hour.

INTRODUCTION

The individual determination of the different phosphorus oxoacids has been addressed by using both batch and continuous methods, most of which rely on the formation of a heteropolyacid with molybdenum as derivatizing reagent, which follows prior to hydrolysis when the analyte is a condensed orthophosphate form. In this way, phosphorous species have been determined in various matrices (soils, plants [1–9]) without special problems, while mixtures of condensed phosphates have been determined globally by segmented flow analysis following hydrolysis at 95°C [10]. Problems in this respect are posed by the individual determinations of these analytes in mixed samples; such is the case with products used by the detergent industry, which require very frequent monitoring and control of the ratio between the four components that make the intermediate manufactured product, namely ortho-(P_1), pyro- (P_2), tripoly- (P_3) and trimeta-(P_4) phosphate. The prior separation of the analytes required can be accomplished by ion chromatography using 0.23 *M* potassium chloride as eluent, but takes as long as 48 min per analysis [11] with samples containing similar concentrations of the analytes ($1 \cdot 10^{-4}$ *M*). The gradient elution technique and ion-exchange chromatography, used in conjunction with a Technicon Autoanalyzer, allow resolution of phosphate mixtures in detergents, but are rather time-consuming (90 min per analysis) [12].

Post-column derivatization by formation of heteropolyacids has been performed on different mixtures by using flow systems with continuous mixing of the reagent and chromatographic eluate. Thus, orthophosphonate and polyphosphate were determined after chromatographic separation, hydrolysis at 140°C and derivatization, which resulted in an analysis time of 15 min, but only for similar amounts of the analytes. Enzymatic hydrolysis allowed development of an easier yet more expensive procedure that was applied to the determination of ortho-, pyro- and tripolyphosphate by isocratic elution with 0.2 *M* potassium chloride in 20 min [13].

In this work we developed a method based on the use of ion-exchange chromatography, gradient elu-

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tion, hydrolysis and derivatization under optimal conditions for the resolution of polyphosphate mixtures in ratios typical of intermediate materials used in detergent manufacture, which requires the intermediate step to be performed with a P_3 content as high as possible and the content of the minor components (P_1, P_2, P_4) to be known in order to control the process. Therefore, both P_3 and the other components must be determined precisely.

EXPERIMENTAL

Reagents and solutions

The eluent consisted of 0.1 or 0.2 *M* potassium chloride containing 1 m*M* Na_4EDTA and adjusted to pH 9.0 with sodium hydroxide. A hydrolysis solution composed of 3 *M* sulphuric acid, 5% (w/v) sodium molybdate in 3 *M* sodium hydroxide and 2% (w/v) ascorbic acid was used. The standard sample contained 1% orthophosphate, 5% pyrophosphate, 92% tripolyphosphate and 2% trimetaphosphate, referred to 100% polyphosphate, plus 1.6% sodium sulphate, 250 ppm sodium fluoride and 1.2% sodium chloride as impurities.

Instruments and apparatus

The chromatographic system was made up of a Hewlett-Packard 1050 high-pressure pump with quaternary gradient, a Rheodyne 7125 injection valve, an Ion-120 ion chromatographic column (120 × 4.6 mm I.D., 100 μequiv./g equivalent capacity) and an Ion-Guard GA-100 anion-exchange pre-column. The post-column system consisted of a Gilson Minipuls-2 peristaltic pump, a UV–visible spectrophotometer equipped with a Hellma 178.12QS flow cell (inner volume 18 μl), three connectors and PTFE tubing of 0.5 mm I.D. A Selecta thermostat filled with Vaseline oil and another furnished with a laboratory-made thermostating chamber were also used.

Sample preparation and procedure

The weighed sample was dissolved in 0.1 *M* potassium chloride. Aliquots of the resulting solution were injected into the system (Fig. 1) and driven to the pre-column for removal of interferences that might reduce the effectiveness of the chromatographic column; the eluent was merged with a 3 *M* sulphuric acid stream at point a, after which the mixture was heated at 90°C in a thermostatic bath filled with Vaseline oil. As the derivatizing reaction developed optimally at room temperature, a cooling recirculating system was used to heat the stream at a suitable temperature for development of this reaction in L_2 after merging with the derivatizing reagents (an on-line mixture of ascorbic acid and sodium molybdate in a basic medium for partial neutralization of the eluent). The reaction product was monitored photometrically at 820 nm. The pressure inside reactor L_3 avoided the formation of bubbles in the system owing to the high temperature achieved by circulating the sample through L_1.

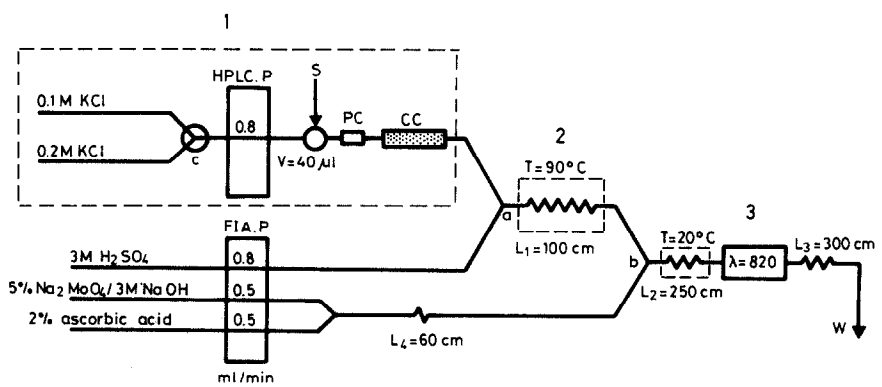

Fig. 1. Configuration for the determination of polyphosphates in intermediate products for detergent manufacture. 1 = clean-up and separation steps; 2 = hydrolysis; 3 = derivatization; c = gradient unit; P = pump; S = sample; PC = pre-column; CC = chromatographic column; a and b = confluence points; W = waste.

RESULTS AND DISCUSSION

Inasmuch as the aim of this work was to develop a method for analysis of intermediate materials used in detergent manufacture, real samples of this type were used to optimize the working conditions and to adapt them to the rather different concentrations at which the analytes are present in them. Both chromatographic variables and those typical of the post-column system were optimized by the univariate method.

Optimization of the chromatographic system

Various eluents (acetic acid–sodium acetate, sodium chloride, potassium chloride) were checked in a preliminary study. The best for our purpose (well defined peaks and short elution times) was found to be potassium chloride. The influence of the eluent flow-rate was studied between 0.6 and 1.2 ml/min. Acceptable resolution was achieved at 0.8 ml/min. Higher flow-rates gave rise to peak overlap, while lower values lengthened the analysis time unduly. Concentrations of potassium chloride ranging from 0.1 to 0.4 *M* were assayed. Increasing salt concentrations resulted in decreasing retention times and hence in growing peak overlap. Under isocratic conditions, the best resolution was achieved with 0.1 *M* potassium chloride, but the resulting analysis time was 30 min; the elution sequence was P_1, P_2, P_3 and P_4. The chromatogram obtained under isocratic conditions with 0.1 *M* potassium chloride reflects adequate separation between P_1, P_2 and P_3, but rather a lengthy separation between P_3 and P_4, which makes the overall analysis time too long. The long elution time required by P_4 results in a high dispersion. This, together with the low concentration of this analyte, gave rise to a wide, low peak. The most suitable gradient was found to be that created by changing the eluent concentration from 0.1 to 0.2 *M* 5 min after injection, followed by another change from 0.2 to 0.1 *M* potassium chloride 9 min after injection. The elution time of the chromatogram obtained under these conditions was shortened from 30 to 15 min. The peaks heights changed linearly ($5 \cdot 10^{-3}$ a.u./μl) with the injected volume over the range 20–180 μl. We chose an injected volume of 40 μl, which ensured adequate sensitivity for the analyte concentrations in the samples. However, the sensitivity can be augmented at will by using larger injected volumes. The effect of the eluent pH was investigated between 7 and 10. The maximum peak resolution and height were obtained at pH 9.0.

Optimization of the post-column system

The hydrolysis step implemented to convert the polyphosphates into orthophosphates was enacted with hot sulphuric acid. By merging the eluate with 3 *M* sulphuric acid (flow-rate 0.8 ml/min) at point a and keeping reactor L_1 at 90°C, the hydrolysis yield achieved was 30% for P_3 and P_4 and 65% for P_2, *i.e.* more than adequate for the sample studied. The optimal length of L_1 was 10 m. Shorter lengths resulted in inadequate hydrolysis, whereas longer lengths resulted in increased hydrolysis efficiency but also in dramatically increased eluate dispersion.

The derivatization reaction involved formation of a heteropolyacid with molybdate and reduction of complexed molybdenum (VI) to molybdenum (V) by ascorbic acid. The optimum temperature for this reaction was between 15 and 30°C, which required the stream emerging from L_1 to be cooled. This was accomplished by using a device that was designed and constructed in our laboratory where the cooled water entered a chamber through a cylinder around which reactor L_2 was coiled; thus, the fluid held in the length of L_2 in contact with the cylinder was first cooled and then used to fill the remainder of the chamber, which was left through the top. The optimum concentration of complexing agent (sodium molybdate) and reducing agent (ascorbic acid) was 5 and 2%, respectively; they were included in separate solutions that were mixed prior to merging with the main stream. As the optimum pH for development of the derivatizing reaction was 0.9, the sodium molybdate solution was prepared in 3 *M* sodium hydroxide: such pH was accomplished by mixing along reactor L_2, the optimum length of which was 250 cm. The effect of the overall flow-rate of the continuous post-column manifold was studied by changing it between 1.0 and 2.5 ml/min while keeping the flow-rate ratio between the three channels as follows: 3/4 q(sulphuric acid) = q(sodium molybdate) + q(ascorbic acid), the last two being equal. The best overall flow-rate was found to be 1.5 ml/min.

Under the above optimal working conditions, bubbles wer formed along the system that yielded

TABLE I

CONCENTRATION OF THE ANALYTES IN THE STANDARDS

Sample	Concentration (g/l)			
	P_1	P_2	P_3	P_4
1	0.005	0.025	0.460	0.010
2	0.010	0.050	0.920	0.020
3	0.025	0.125	2.300	0.050
4	0.050	0.250	4.600	0.100
5	0.100	0.500	–[a]	0.200
6	0.200	1.000	–[a]	0.400
7	0.400	2.000	–[a]	0.800

[a] Beyond the capacity of the detector.

parasitic signals on arrival at the flow cell. A suitable length of tubing after the flow cell created an overpressure in the continuous manifold that prevented the bubbles from circulating freely and thus reaching the detector. A length of 300 cm was sufficient for this purpose.

Calibration curves

Calibration curves were obtained by running different standard mixed solutions made by direct weighing and diluting them with the mobile phase. The weight of standard for each solution (expressed as weight/volume percentage) and the concentration of each analyte in the samples are listed in Table I. The concentration of tripolyphosphate in standard samples 5–7 was beyond the capacity of the photometric detector. Peak-height data were used to establish equations relating this parameter to the concentration of the corresponding analyte.

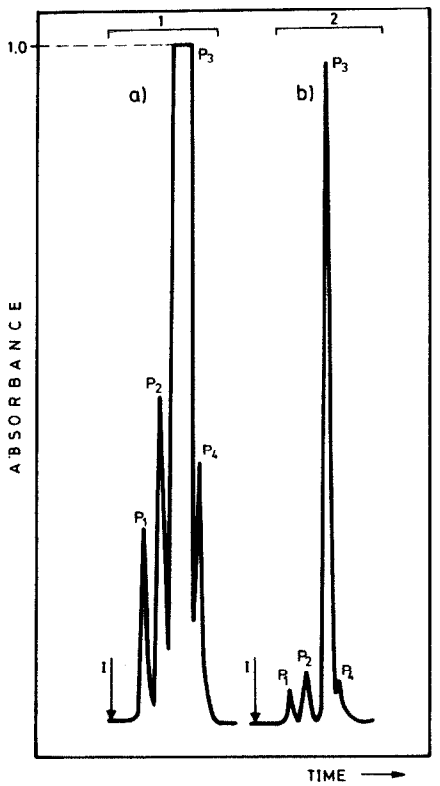

Fig. 2. Chromatograms obtained by gradient elution. 1 = 2% (w/v) dilution; 2 = 0.2% (w/v) dilution.

Such equations, their regression coefficients and relative standard deviations (R.S.D.) each analyte are listed in Table II.

Application of the method to real samples

The differences in concentrations of the analytes in the samples required two dilutions to be made in

TABLE II

FEATURES OF THE CALIBRATION CURVES

Analyte	Equation[a]	Regression coefficient	R.S.D. (%)
Orthophosphate	$A = 0.0082 + 1.0505\ [P_1]$	0.9967	2.5
Pyrophosphate	$A = 0.0136 + 0.3377\ [P_2]$	0.9985	3.2
Tripolyphosphate	$A = 0.1331 + 0.3079\ [P_3]$	0.9958	1.9
Trimetaphosphate	$A = 0.0168 + 0.6621\ [P_4]$	0.9963	3.0

[a] A = absorbance units; concentration in g/l.

order to be able to determine the four phosphates precisely. A 2% (w/v) solution for the determination of minor components and a 0.2% (w/v) solution for the major components were used. The recordings shown in Fig. 2 were obtained by injecting sequentially the two samples into the overall configuration (Fig. 1). Three different samples supplied by a national industry that manufactures the intermediate products were analysed; the results obtained are consistent with those of the analysis made at the factory laboratory (chromatographic separation in a flow-pressure column followed by derivatization with sodium molybdate–ascorbic acid in a segmented-flow analyser).

CONCLUSIONS

The use of ion chromatography and gradient elution in addition to an optimized post-column manifold and chemical variables involved in the post-column steps allowed us to develop an efficient method for the determination of the four most common phosphates present in intermediate material used for detergent manufacture with clear advantages over previous methods such shorter analysis times, a simpler post-column system [13], milder hydrolysis conditions [14] and lower analytical costs [15]. The optimization of the proposed method for the presence and concentration ratios of these four analytes is also a novelty that makes it directly implementable by industries devoted to detergent or intermediate product manufacture.

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