Heat treatment effect on polyphosphate chain length in aqueous and calcium solutions

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ABSTRACT

Polyphosphate blends are used in food such as meat and dairy products to improve their texture and stability by sequestering metal ions. This study aims to analyse the impact of high temperature treatments on the composition of polyphosphates with regards to phosphate chain length in aqueous solutions with or without calcium. Temperature treatments of 120 °C for 10 min led to the hydrolytic degradation of long-chain phosphates into orthophosphate and trimetaphosphate whereas heating the salts to 100 °C in aqueous solutions had little effect on their composition. The presence of calcium increased the hydrolysis rate of long-chain phosphates and led to more trimetaphosphate and pyrophosphate as end products. The evolution of emulsifying salts' composition under heat treatment may lead to a modification of their chelating properties since short-chain phosphates are less efficient to chelate calcium than long-chain phosphates.

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1. Introduction

Through their sequestering and pH displacement action, polyphosphates are used in agri- and agro-industry products such as fertilizers, water-softening agents, meat, fish and dairy products. Polyphosphate blends improve texture and emulsion stability of meat products (Anjaneyulu, Sharma, & Kondaiah, 1990; Shahidi & Synowiecki, 1997) and increase their shelf life due to their antioxidant properties (Allen & Cornforth, 2009). These additives also represent a major ingredient in processed cheese. By sequestering calcium, they cause protein dispersion and hydration, thereby producing a homogeneous processed cheese emulsion (Caric, Gantar, & Kalab, 1985; Lee & Anema, 2009; Mizuno & Lucey, 2005).

Polyphosphate emulsifying salts are made of condensed phosphates containing various chain lengths. According to temperature, pH or ionic environment, the proportion of each chain length does not remain constant due to the occurrence of hydrolysis reactions (McBeath, Lombi, McLaughlin, & Bumann, 2007). Studying the hydrolysis of condensed phosphates is interesting from an industrial point of view since the ultimate reversion product, orthophosphate, has not the same sequestering properties as polyphosphates (Crowther & Westman, 1954).

Hydrolysis of polyphosphates in aqueous solutions at neutral pH is very slow when solutions are heated at temperatures below 100 °C (Bell, 1947; Halliwell, McKelvie, Hart, & Dunhill, 2001; Torres-Dorante, Claasen, Steingrobe, & Olfs, 2005). However, condensed phosphates are used in sterilised food products such as processed cheese, which are cooked at 120 °C or more, at a pH around 5.6. The impact of such temperatures on condensed phosphates in these pH conditions has not yet been studied. Moreover, emulsifying salts are often used in food products containing alkaline earth metal ions such as calcium. Cations are strongly complexed by condensed phosphates and seem to modify kinetics of hydrolysis reactions, but their impact on hydrolysis reactions has never been clearly presented (Van Wazer, Griffith, & McCullough, 1955).

Most investigations on polyphosphate degradation are based on measuring the rate of orthophosphate formation (McBeath et al., 2007). This approach does not supply information about the changes in polyphosphate composition with regard to their chain lengths.

However, ion chromatography gives information on the proportion of each condensed phosphate form in polyphosphate mixtures containing different chain lengths (Baluyot & Hartford, 1996; Halliwell et al., 2001; McBeath et al., 2007; Watanabe, Sato, & Saito, 1975). This analytical technique has been used in this work to study the composition of short-chain phosphates (sodium orthophosphate, sodium pyrophosphate, sodium triphosphate

and sodium trimetaphosphate), and long-chain phosphates (Graham's salt and a commercial polyphosphate), in an aqueous solution at pH 5.6. The composition of these different salts has been studied in the presence of calcium at 20 °C and after heat treatment of 10 min at 100 and 120 °C, respectively.

The aim of this study is to analyse the impact of heat treatments above 100 °C on polyphosphate composition in aqueous solutions in the presence or absence of calcium.

2. Materials and methods

2.1. Reagents

Di-sodium hydrogen phosphate (HNa_2O_4P), sodium pyrophosphate decahydrate ($Na_4P_2O_7$, $10H_2O$), sodium tripolyphosphate ($Na_5P_3O_{10}$), trisodium trimetaphosphate ($Na_3P_3O_9$) and sodium hexametaphosphate (Graham's salt-$(NaPO_3)_n$) were purchased from Sigma Aldrich (Steinheim, Germany). Sodium polyphosphate (BK Giulini GmbH, Ladenburg) used as emulsifying salt was of commercial grade.

De-ionised water was prepared in a Milli-Q water purification system. All other chemicals and reagents were of the HPLC/analytical grade.

2.2. Preparation of polyphosphate solutions and temperature treatments

Aqueous solutions of emulsifying salts were prepared by dissolving each salt in de-ionised water at a concentration of 0.5% (w/w) of anhydrous salt. Solutions were adjusted at pH 5.6 with HCl 2.5 N or NaOH 0.1 N and kept 2 h at 20 °C before temperature treatments.

Calcium solutions of emulsifying salts were prepared with the same procedure. $CaCl_2$ at 0.1% (w/w) was added prior to emulsifying salt addition. The ratio calcium/emulsifying salt was approximately the same as the one encountered in food products such as processed cheese.

Temperature treatments were (1) 20 °C (Control solutions) (2) 10 min at 100 °C in a water bath and (3) 10 min at 120 °C in an autoclave. Solutions were then cooled to room temperature and analysed within 24 h. Each treatment was duplicated.

2.3. Speciation and quantification of polyphosphates

2.3.1. Preparation of working solutions

The pH of each solution was checked at 20 °C before ion chromatographic methods. The pH ranged between 5.5 and 5.7 except for Graham's salt in water after 120 °C heat treatment (pH 4.9), pyrophosphate in calcium solution after 100 °C treatment (pH 5.3) and for Graham's salt, trimetaphosphate and commercial polyphosphate in calcium after 120 °C treatment (pH 5.0; 5.1 and 5.3, respectively).

All solutions were diluted by a factor of 1:1000 and then filtered through 0.2 μm (PALL GHP Acrodisc 13 mm).

2.3.2. Ion chromatography system

A Dionex ICS 2500 chromatography system, equipped with a GP50 Gradient pump, an ED50 Pulsed Electrochemical Conductivity detector, a DS3 Conductivity Cell and an AS 50 automated sampler was used for all analyses. The Anion Self-Regenerating Suppressor ASRS® 300–4 mm was operated in the auto-suppression recycle mode. The data acquisition and instrument control were performed using Dionex chromeleon 6.8 software.

The 4 × 50 mm guard and 4 × 250 mm analytical columns used in this work were the Dionex IonPac® AGll HC and IonPac® ASll,

Table 1
Ionic chromatography gradient program.

Time (min)	NaOH 200 mM (%)	Degassed deionised water (%)
0	10	90
0.1	10	90
40	70	30
47	70	30
48	10	90
60	10	90

respectively. A Dionex anion trap column (ATC-3 IonPac) was placed between the eluent pump and the injection valve.

2.3.3. IC operating procedure

The 60-min gradient program was increased from 20 to 140 mM NaOH over an initial 47-min period as described in Table 1. A constant flow rate of 1 ml/min was used with an injection volume of 50 μl. This method was adapted according to the procedure presented by Baluyot and Hartford (1996).

2.3.4. Quantification of polyphosphates

Standard solutions of di-sodium hydrogen phosphate, sodium pyrophosphate decahydrate, sodium tripolyphosphate and trisodium trimetaphosphate were prepared at 0.001%, 0.002% and 0.005% (w/w) of phosphorus oxide. A linear relationship between the peak area and the concentration in phosphorus was established for these salts. As no polyphosphate > P3 (tripolyphosphate) was commercially available, the peak area for long chain phosphates was also considered to be proportional to their concentration.

The proportion of each phosphate species for each salt was calculated by dividing the detected area for the specific species by the total areas detected for the salt.

2.4. Statistical analysis

Analysis of variance (ANOVA) was performed with the analysis of least significance differences at the 5% level to discriminate between treatments.

3. Results and discussion

3.1. Hydrolysis of polyphosphates at high temperatures in water

3.1.1. Short-chain polyphosphates

Heat treatments of 100 and 120 °C during 10 min were applied on aqueous solutions containing short-chain phosphates. Fig. 1 compared the proportion of each phosphate species in these heat treatment conditions to 20 °C samples.

Several studies reported a very slow hydrolytic degradation of polyphosphates in aqueous solutions at room temperature (Halliwell et al., 2001; Van Wazer et al., 1955). McBeath et al. (2007) showed that the half life of triphosphate at pH 5.4 was 175 days. Thus, it was considered that no hydrolysis occurred in solutions at 20 °C (control solutions).

Heat treatment did not change the composition of orthophosphate solutions (results not shown). No condensation reaction was observed.

In pyrophosphate and trimetaphosphate solutions, no hydrolysis occurred after 10 min at 100 °C whereas 5% of triphosphate was transformed into pyrophosphate in tripolyphosphate solutions. Van Wazer et al. (1955) showed that pyrophosphate was more resistant to hydrolytic degradation than triphosphate since its ions were symmetrical both in charge and atomic position. This tendency was confirmed at 120 °C since triphosphate was the only salt to be totally hydrolysed, mainly into orthophosphate. However,