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Journal of Chromatography A, 769 (1997) 349–351

JOURNAL OF CHROMATOGRAPHY A

Short communication

Capillary electrophoresis of longer-chain polyphosphates

Frederick S. Stover

Performance Materials Technology, Monsanto Company 800 N. Lindbergh Blvd. St. Louis, MO 63167, USA

Received 15 October 1996; revised 10 January 1997; accepted 13 January 1997

Abstract

Capillary electrophoretic separations of sodium polyphosphates with anion chain lengths from 1 to >30 are presented. A buffer containing pyromellitic acid, triethanolamine and hexamethonium hydroxide gives a high resolution separation of linear and cyclic polyphosphate species. Distinct separation patterns can be obtained in 20 min for glassy sodium phosphates with number-average chain lengths from 5 to 44. The preliminary electrophoretic separations presented here should be useful for the rapid characterization of complex polyphosphate mixtures.

Keywords: Polyphosphates; Sodium phosphate glass

1. Introduction

Glassy sodium phosphates [1] are amorphous salts containing highly condensed, polymeric phosphate anions. Commercial sodium polyphosphates with average degrees of polymerization from ~10 to 25 are useful as food ingredients and in water treatment [2]. The most common characterization of these materials involves pH titration for number-average chain length [3]. Methods for determining polyphosphate species distributions include paper chromatography [4], high-performance liquid chromatography [5] and, most recently, ion chromatography with suppressed conductivity detection [6,7].

Capillary electrophoresis (CE) has been employed for the separation of smaller polyphosphates with chain lengths of 2–4; pyro-, tripoly-, tetrapoly- and cyclic trimetaphosphate [8–10]. We describe here preliminary CE separations of longer-chain sodium polyphosphates with chain lengths ≥5. Use of a divalent electroosmotic suppression reagent (hexamethonium hydroxide) and pyromellitate for indirect UV detection, provides a rapid, high-resolution separation of longer-chain polyphosphates.

2. Experimental

2.1. Chemicals and materials

A commercially available buffer (IonPhor Anion PMA Electrolyte Buffer; Dionex, Sunnyvale, CA, USA) was used for this study. Hexamethonium bromide was obtained from Sigma (St. Louis, MO, USA), as were sodium ortho-, pyro-, tripoly-, and trimetaphosphates, and ammonium tetrapolyphosphate. Hexamethonium hydroxide (HMOH) was prepared by passing a 50 m*M* aqueous solution of the bromide salt through an anion-exchange cartridge (OnGuard-A, Dionex) in the hydroxide form. Glassy sodium phosphates were commercial products or experimental samples obtained from Monsanto (St. Louis, MO, USA). Average chain lengths of these

PII S0021-9673(97)00070-8

sodium polyphosphates were determined using standard pH titrations [3].

2.2. Instrumentation

CE was performed on a SpectroPhoresis 500 instrument (Thermo Separation Products, San Jose, CA, USA) equipped with a 44 cm long (36 cm effective length)×75 μm I.D. fused silica capillary. Separations were run at −20 kV and 25°C using indirect UV detection at 254 nm.

2.3. Procedure

The following sequence of capillary conditioning steps was performed for 5 min each prior to runs made with a new buffer: (1) 0.5 *M* NaOH, (2) deionized water, (3) 50 m*M* HMOH and (4) running buffer. An initial run of 1.0 mg/ml orthophosphate standard was performed prior to polyphosphate separations. Polyphosphate samples were diluted in deionized water to 0.2–0.5 mg/ml and injected by vacuum for 2 s. A fresh buffer vial was used for a 2 min wash after each run, and for the subsequent separation.

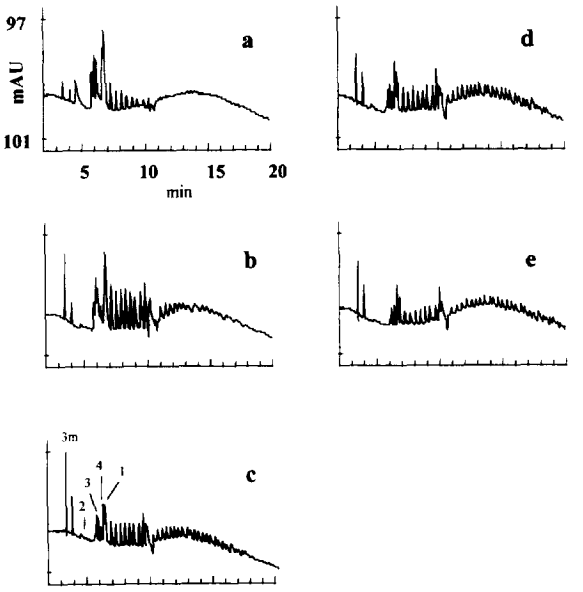

Fig. 1. Separations of sodium polyphosphates with average chain lengths of (a) 5.6, (b) 11.4, (c) 17, (d) 22 and (e) 44. Sample concentrations are (a) 0.2 mg/ml, and (b–e) 0.5 mg/ml. Commercial buffer; 2.25 m*M* pyromellitic acid, 1.6 m*M* triethanolamine, 0.75 m*M* HMOH, 6.5 m*M* NaOH, pH 7.7. (c) shows verified peak identities where the number is chain length (number of phosphorus atoms) with "m" indicating meta species. Absorbance and time axes for (b–e) same as (a).

3. Results and discussion

Fig. 1 shows typical separations obtained for sodium polyphosphate samples with varying average chain length using the commercial buffer at pH 7.7. Clearly distinct separation patterns for polyphosphates with different average chain length are observed. Longer chain length polyphosphates display a shift toward longer migration times. From the general shape of the separations, CE appears valuable for approximating average chain lengths ($\bar{n}$) in the 5–45 range.

Assignments of peak identity are given in Fig. 1c for the $\bar{n}=17$ polyphosphate separation. Ortho- (1), pyro- (2), tripoly- (3), trimeta- (3m) and tetrapolyphosphate (4) migration times were verified by spiking pure standards into the diluted polyphosphate solutions. Other peak identities can be inferred from known distributions obtained by ion chromatography [6] or HPLC [5]. The most likely assignments for other peaks are (1) tetrametaphosphate for the sharp peak at ~4 min migration time, (2) $n\approx6$–12 polyphosphates at migration times of 7–9 min and (3) $n\approx15$–30 polyphosphates at migration times of 10–15 min. Total verification of all peak identities is not necessary to use CE as a qualitative tool for polyphosphate identification. Despite unknown quantitative response factors, ratios of short- vs. long-migration time peaks, or vs. meta peaks, from these separation should be useful in classifying polyphosphates.

Harekuwe and Haddad [11] recently described the variation in phosphate response vs. capillary conditioning procedure, and ascribed these changes to competitive adsorption between phosphate and EOF modifier on the capillary surface. We have found that the conditioning procedure described in the Section 2 gives sufficient within-day and between-day reproducibility for our uses, i.e. to confirm the polymeric nature of a phosphate sample and to estimate average chain length.

Previous isotachophoretic analysis [12] indicated

that polyphosphates of chain length ≥4 display nearly equal free solution electrophoretic mobilities. The basis for the separations shown here is thought to involve ion-pairing between the cationic EOF modifier and the polyphosphates. Similar interactions between polycations with small anions have been exploited for "ion-exchange" electrophoretic separations of aromatic sulfonates [13] and substituted benzoates [14]. We have performed preliminary polyphosphate separations using other EOF modifiers (dodecyltrimethylammonium and diethylenetriamine), and have seen a significant effect of EOF modifier identity on the separation patterns. Further work is planned to better assess the mechanism of these polyphosphate separations, and to optimize analytical performance.

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