Available online at www.sciencedirect.com
ScienceDirect
Journal of Chromatography A, 1125 (2006) 189–194
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Fast and high-resolution ion chromatography at high pH on short columns packed with 1.8 μm surfactant coated silica reverse-phase particles

Sarah Pelletier, Charles A. Lucy *

Department of Chemistry, Gunning/Lemieux Chemistry Centre, University of Alberta, Edmonton, Alta. T6G 2G2, Canada

Received 18 April 2006; received in revised form 17 May 2006; accepted 19 May 2006
Available online 19 June 2006

Abstract

Rapid ion chromatographic separations of small inorganic anions are performed on columns packed with high-pH resistant Zorbax Extend-C18 1.8 μm silica particles. Seven anions (iodate, chloride, nitrite, bromide, nitrate, phosphate, sulphate) are separated with 1.3 and 2 cm long × 0.46 cm I.D. C_{18} columns coated with the surfactant didodecyldimethylammonium bromide (DDAB). A 40 s separation is achieved at 2 mL/min with a 2.5 mM 4-hydroxybenzoic acid eluent at pH 10. Finally, the DDAB removal procedure is improved to eliminate the pressure build-up caused by precipitation of the surfactant in the column upon uncoating.

Keywords: Ion chromatography; Inorganic anions; DDAB; Didodecyldimethylammonium bromide; Fast separations; High pH; Extra-column band broadening

1. Introduction

Over the past few decades, ion chromatography (IC) has developed into a significant chromatographic technique and has found numerous applications within the fields of environmental and clinical analyses, as well as in the semiconductor, food and beverage, and pharmaceutical industries [1]. As for any determination, reducing the analysis time is a significant goal; leading to improvements in sample throughput, productivity and cost. Ion separations are most commonly performed on anion exchange polymer-based columns (10–25 cm) and require 8–15 min for the determination of 7–10 inorganic anions [1]. Ideally, fast IC separations should take less than 1 min, resolve the same analytes, have comparable detection limits (in the nM range), use flow rates of ≤2 mL/min and employ standard liquid chromatography instrumentation. Recently, high-speed IC methods for anions using packed or monolithic columns have been described in three review papers [2–4].

Fast IC with suppressed conductivity detection has been achieved by converting reverse-phase silica-based columns into ion exchangers by coating the columns with hydrophobic cationic surfactants such as didodecyldimethylammonium bromide (DDAB) or cetyltrimethylammonium chloride (CTAC) [2,5–11]. An advantage of this approach is that the column anion exchange capacity can easily be varied by adjusting the acetonitrile (ACN) content of the surfactant coating solution [9–11].

A few approaches have been explored for fast anion analysis using surfactant-coated columns. Hatsis and Lucy used highly permeable 5 cm long monolithic columns enabling flow rates of 10 mL/min for a separation of seven small inorganic anions in 30 s [10]. On the other hand, the group of Paull demonstrated that 1 cm long monolithic columns can perform separations of five analytes at a much slower and practicable flow rate of 0.4 mL/min [12]. Recently, after careful reduction of extra-column broadening Pelletier and Lucy used 0.5 and 1 cm long monolithic columns to resolve 5–7 anions in 1–2 min with flow rates of 2 mL/min [11].

Reduction of the analysis time in liquid chromatography can also be achieved through the use of short columns packed with small particles. The effect on separation time from combining short columns and small particles in anion chromatography has been shown by Connolly and Paull [7,13,14]. They used 3 cm long columns packed with 3 μm C_{18} silica particles coated with DDAB to separate 9 anions in 3 min at 2 mL/min [7].

A drawback of using silica-based columns for IC is that the eluent is limited to a maximum pH of 7–8 due to the poor chemical stability of silica-based stationary phases in alkaline solutions [15]. In alkaline conditions, nucleophilic attack of the

---

* Corresponding author. Tel.: +1 780 492 0315; fax: +1 780 492 8231.
E-mail address: charles.lucy@ualberta.ca (C.A. Lucy).

0021-9673/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2006.05.059

Si–O bonds by hydroxide results in the formation of $Si(OH)_4$ and erosion of the silica surface [15]. Consequently, when a silica-based column is exposed to elevated pH, its efficiency decreases while the backpressure increases [16]. The speed of particle degradation at high pH depends on many factors, but principally on the nature of the stationary phase, the mobile phase buffer, the nature and content of the organic modifier, and the temperature [15,16]. Traditional IC eluents such as sodium hydroxide and carbonate/bicarbonate, require a pH greater than 10, and so are not compatible with silica columns. Due to the limited pH stability of silica, cyanophenol and 4-hydroxybenzoic acid have been used in past fast IC methods [1,10–12]. However, cyanophenol and 4-hydroxybenzoic acids are weak eluents since they only have a −1 charge at pH below 8. They are thus, not well suited for rapid separations since the retention times of multiply charged analytes are long [1,17]. Furthermore, the low pK_a of these eluents results in a higher conductivity background after suppression, which compromises the limits of detection [1,17].

As demonstrated in the above paragraphs, the merits of speed, resolution, sensitivity and convenience of an ideal fast anion chromatography method have not yet been united into one single method. The new Zorbax Extend-C18 silica-based phase manufactured by Agilent Technologies (Palo Alto, USA) is stable from pH 2–11.5 and recently became available in 1.8 μm particles. These phases feature a bidentate linkage of the bonded C_{18} phase which protects the silica structure from nucleophilic attack thus enhancing stability at elevated pH [18,19]. In this work we use 1.3 and 2.0 cm long columns packed with 1.8 μm Extend particles for anion separations using 4-hydroxybenzoic acid and carbonate/bicarbonate eluents between pH 5.6 and 10.5. Through control of the extra column broadening effects and the use of a 4-hydroxybenzoic acid eluent at high pH, 7 analytes are resolved in 40 s at 2 mL/min using a conventional liquid chromatography system.

2. Experimental

2.1. Apparatus

A model 625LC Waters (Milford, MA, USA) HPLC pump was used to deliver the eluent. A 0.5 μm stainless steel frit (Upchurch, Oak Harbor, WA, USA) and a pre-column [11] (Zorbax Extend-C18, 1.25 cm long × 0.46 cm I.D., 5 μm particles, Agilent Technologies, Palo Alto, CA, USA) were positioned before the injector. The pre-column was coated with didodecyldimethylammonium bromide as described in Section 2.3. The pre-column was added to the system to improve the stability of the retention times. DDAB leaching from the analytical column was continuously replaced by DDAB leaching from the pre-column [11]. A Rheodyne (Berkeley, CA, USA) injection valve (model 7520) with a 1 μL loop injected samples onto the Zorbax Extend-C18 1.8 μm particle column (1.3 or 2 cm long × 0.46 cm I.D., Agilent Technologies) also coated with DDAB. The 2.0 cm long column is a standard length commercially available from Agilent. The 1.3 cm long column was graciously custom packed for us by Bill Barber of Agilent Technologies. The column was connected directly to the injection valve through a column coupler (Merck, Darmstadt, Germany) which was fitted with 3 cm of 0.004 in. I.D. PEEK tubing (Upchurch). A Dionex (Sunnyvale, CA, USA) Anion Atlas Electrolytic Suppressor (AAES, 35 μL void volume) or a Dionex Anion Self Regenerating Suppressor-2 mm (ASRS ULTRA II 2 mm, 15 μL void volume) was connected to the column with 5 cm of PEEK tubing (0.004 in. I.D., Upchurch). In addition, a modified ASRS ULTRA II 2 mm suppressor capable of sustaining eluent flow rates of 2 mL/min was provided by Dionex. Compared to a standard suppressor, this suppressor had narrower internal channels which facilitated a better seal owing to a larger gasket area. The suppressors were operated in the external water mode with eluent flow rates of 1 or 2 mL/min and a regenerant flow rate of ∼2 mL/min. (The suppressors were removed during DDAB coating or uncoating of the columns and during flushing of the carbonate eluent in Section 3.1.2.)

A Dionex ED-50A electrochemical detector was used for detection. A 10 cm × 0.004 in. I.D. PEEK tubing (Upchurch) connected the column or suppressor directly to the cell, which was within a temperature controlled enclosure (DS3-1 Detection Stabilizer, Dionex). The conductivity cell volume was 1 μL, the rise time was 0.05 s and data was collected with the PeakNet 5.2 software (Dionex) at 20 Hz. A Dionex Variable Wavelength Detector-II was used at 254 nm to perform RPLC column tests. The UV cell was 9 μL, had a 6 mm optical path length and the rise time was 1 s.

A Corning 445 pH-meter (Corning, New York, NY, USA) with a Corning electrode (3 in 1 Combo P/N 476436) was used for pH measurements.

2.2. Reagents and solution preparation

All solutions were prepared in deionised 18 MΩ water (Nanopure Water System, Barnstead, Chicago, IL, USA). Chemicals were reagent grade or better. The sodium salts of chloride (EMD Chemicals, Gibbstown, NJ, USA), nitrite (BDH, Toronto, Canada), nitrate (ACP Chemicals, Montreal, Canada), sulphate (BDH) and phosphate ($NaH_2PO_4{\cdot}H_2O$, EMD) were used. Potassium salts of bromide (Fisher, Fair Lawn, NJ, USA) and iodate (ACP Chemicals) were used. In addition, sodium bromide (Anachemia, Montreal, Canada) solution was used in these experiments to rinse the columns prior to removal of the DDAB coating.

IC eluents were freshly prepared by dissolving the appropriate amount of 4-hydroxybenzoic acid (99%, Aldrich, St. Louis, MI, USA) in water, adjusting the pH with a 2.5 M and 1.0 M sodium hydroxide (Fisher) solution and diluting with water to the desired volume. Carbonate eluents were prepared by dissolving the appropriate amounts of sodium carbonate and sodium bicarbonate (EM Science, Gibbstown, NJ, USA) in water. The solutions were filtered through 0.22 μm Magna nylon membrane filters (GE Osmonic, Trevose, PA, USA) prior to use. To avoid chloride contamination from the pH electrode, the pH of an aliquot of the final solutions was measured.

The column coating solution was 1 mM didodecyldimethylammonium bromide (98%, Aldrich) in 35% or 40% v/v acetonitrile (ACN, HPLC grade, Fisher). The appropriate amount