



Utilization of a diol-stationary phase column in ion chromatographic separation of inorganic anions

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ARTICLE INFO

Article history:

Received 24 August 2012

Received in revised form 26 October 2012

Accepted 29 October 2012

Available online 3 November 2012

Keywords:

Non-suppressed ion chromatography
Diol-stationary phase
Anion-exchange
Inorganic anions
Acidic eluent

ABSTRACT

We describe the ion chromatographic separation of inorganic anions using a diol-stationary phase column ($-\text{CH}(\text{OH})\text{CH}_2\text{OH}$; diol-column) without charged functional groups. Anions were separated using acidic eluent as in typical anion-exchange chromatography. The retention volumes of anions on the diol-column increased with increasing H^+ concentration in the eluent. The anion-exchange capacities of diol-columns in the acidic eluent (pH 2.8) were larger than that of zwitterionic stationary phase column but smaller than that of an anion-exchange column. The separation of anions using the diol-column was strongly affected by the interaction of H^+ ions with the diol-functional groups and by the types of the eluents. In particular, the selection of the eluent was very important for controlling the retention time and resolution. Good separation was obtained using a diol-column (HILIC-10) with 5 mM phthalic acid as eluent. The limits of detection at a signal-to-noise ratio of 3 ranged from 1.2 to 2.7 μM with relative standard deviations (RSD, $n = 5$) of 0.04–0.07% for the retention time and 0.4–2.0% for the peak areas. This method was successfully applied to the determination of H_2PO_4^- , Cl^- , and NO_3^- in a liquid fertilizer sample.

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1. Introduction

Ion chromatography (IC) has been a widely employed technique for the determination of ionic compounds [1–4] since its introduction in 1975 [5]. Most stationary phases employed in IC have functional groups with charged or chargeable moieties with which ionic analytes undergo electrostatic attractive/repulsive interactions [6].

Along with improvements in analytical techniques, the ongoing development of separation columns has produced better resolution, higher numbers of theoretical plates, and higher speed for ion analysis [1]. These efforts have yielded stationary phase columns possessing non-charged or electronically neutral functional groups such as neutral polymers or zwitterionic compounds for application to IC [1,7–28]. For example, Takeuchi et al. achieved the separation of anions by anion-exchange by exploiting the interactions of cationic eluent with polyethylene glycol (PEG), polyoxyethylene (POE), or crown ethers based on ion-dipole interactions [12–16]. In electrostatic ion chromatography (EIC) developed by Hu et al.,

electronically neutral zwitterionic stationary phase, which possesses both negative and positive charges in the same molecule, is used in separation columns. In the EIC, sulfobetaine zwitterionic reagent both physically bonded onto ODS and chemically bonded onto silica gel have been employed in the separation of anions [17–27]. Additionally, hydrophilic interaction liquid chromatographic (HILIC) columns with zwitterionic functional groups have been demonstrated to simultaneously separate anions and cations in active pharmaceutical components by elution with acetonitrile–ammonium formate buffer [24,28].

These examples demonstrate the feasibility of separating anions using stationary phases with uncharged or electronically neutral zwitterion moieties, combining ion-dipole interactions with eluent ions and effects of the stationary phases. These are foundational concepts for advancing the state of separation sciences.

Recently, we discovered that a HILIC-10 column with diol-functional stationary phase could be used to separate anions with excellent resolution using tartaric acid (TAH) as eluent [29]. However, the overall retention time was over 40 min because the diol-column retained the anions so strongly, a factor that could not be successfully controlled in that study. Therefore, characterization of anion retention is necessary in the process of making this technique practical for anion separation.

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The purpose of this study was to optimize the type and concentration of acidic eluent for use with diol-columns for application to IC. The diol-columns (Acclaim HILIC-10 and TSKgel OH-120) were used in order to compare the retentions for anions, anion-exchange capacity, and anion separation using acidic eluent, and the results were compared also to those obtained using anion-exchange (Tosoh TSKgel Super IC-Anion HS) and zwitterionic (SeQuant ZIC-HILIC) columns. We optimized the eluent conditions and confirmed the performance of the system through the separation and determination of anions commonly found in a liquid fertilizer sample.

2. Experimental

2.1. Apparatus

Ion chromatographic separation was performed using a Tosoh IC-2010 ion chromatograph which consisted of a dual pump, an on-line degasser, a column oven, a sample injector, and conductimetric detector. The analytical conditions were as follows: flow rate, 0.8 mL/min; column temperature, 40 °C; and injection volume, 30 μ L.

2.2. Columns

Four different separation columns were employed in this study. Dionex Acclaim HILIC-10 (HILIC-10; 150 \times 4.6 mm i.d.) and Tosoh TSKgel OH-120 (OH-120; 150 \times 4.6 mm i.d.) were used as the representative diol-columns. For comparison, SeQuant ZIC-HILIC (ZH; 150 \times 4.6 mm i.d.) was used as a zwitterionic stationary phase column, and TSKgel Super IC-Anion HS (AS; 100 \times 4.6 mm i.d.) was used as an anion-exchange column. Detailed information on the separation columns is summarized in Table S1 in the Supplementary Information. The columns were equilibrated thoroughly with eluent for 30 min before chromatographic runs.

2.3. Standard and sample preparation

All reagents were of analytical reagent-grade and were purchased from Wako (Osaka, Japan). Solutions were prepared by dissolving them in distilled and deionized water to a concentration of 0.1 M. Dilutions were made using water as necessary. The eluents used were TAH, phthalic acid, salicylic acid, potassium hydrogen phthalate, citric acid, and succinic acid. The standard sample comprised a mixture of inorganic ions (NaNO_2 , MgSO_4 and KCl , or MgSO_4 , CaCl_2 , NH_4NO_3 , KH_2PO_4 , NaClO_4 , NaSCN , KI and NaBr) in aqueous solution, each at a concentration of 0.5 mM.

Liquid fertilizer was purchased from Sumitomo Chemical Garden Products (Japan). The sample was filtered through a 0.45- μ m syringe filter and diluted 1000-fold in water before injection.

2.4. Anion-exchange capacity

The anion-exchange capacities (AECs) of the four different columns were determined by the breakthrough method described by Ueki et al. [30]. They determined the cation-exchange capacity by passing 10 mM CuSO_4 through a cation exchanger-modified monolith column and monitoring UV absorption at 210 nm. In this study, we determined the AEC by passing 5 mM TAH ($[\text{H}^+] = 2.8$ mM) through the columns. The AEC values were calculated from Eq. (1):

$$\text{AEC} = \frac{F \times [\text{H}^+] \times t_{\text{bp}}}{C_v} \quad (1)$$

where F is flow rate (L/min), $[\text{H}^+]$ is H^+ concentration in the eluent (meq/L), t_{bp} is time of the breakthrough point (min), and

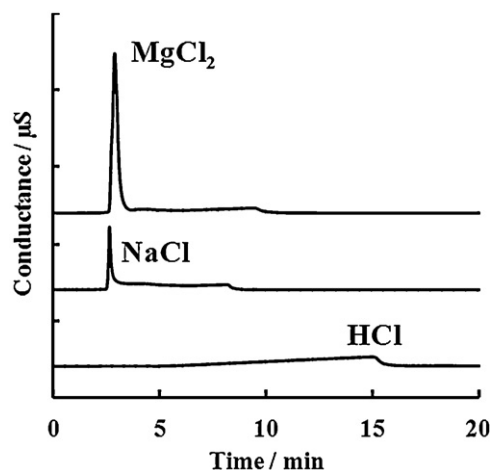


Fig. 1. Chromatograms of acids and salts on the HILIC-10 column using water eluent. Conditions: injected sample concentration, 0.5 mM; flow rate, 0.8 mL/min; column temperature, 40 °C; injection volume, 30 μ L; conductometric detection.

C_v is column volume (L). The detail procedure was described in supplementary information and Fig. S1.

3. Results and discussion

3.1. Retention for salts and acids using water eluent

First, we investigated the retention behaviors of NaNO_2 , MgSO_4 , and KCl on the HILIC-10, OH-120, AS, and ZH columns using water eluent. The analyte salts were poorly separated by the ZH column, which relies on the electrostatic repulsion and attraction of anions to the sulfobetaine zwitterionic stationary phase (Fig. S2) [17]. However, the diol-column could not separate analyte salts using water eluent, meaning that the stationary phase did not retain ions under these conditions as is the case in typical anion-exchange chromatography.

Likewise, separation was not achieved for a sample composed of HCl , HNO_3 , and H_2SO_4 injected into the diol-columns. However, the retention times for acids were longer and the peak shapes were broadened as compare to the peaks obtained for the salts NaCl and MgCl_2 , as shown in Fig. 1. A similar behavior was observed when acids were injected into the ZH column, which also strongly retained acidic compounds [26]. Stronger retention for acids as compared to salts was observed for both the HILIC-10 and OH-120 columns.

3.2. Anion-exchange capacity

Subsequently, the anion-exchange capacities (AECs) of the four different columns were determined by the breakthrough method described in supplementary information. In this study, we determined the AEC by passing 5 mM TAH ($\text{pH} = 2.8$) through the columns. The AEC values calculated from Eq. (1) were the order AS (6.1 meq/L) > HILIC-10 (5.4 meq/L) > OH-120 (2.3 meq/L) > ZH (0.63 meq/L).

3.3. Retention behaviors of inorganic ions

We investigated the retention behaviors of inorganic ions using acidic eluent (5 mM TAH) with the four different columns. The sample injected was a mixture of MgSO_4 , CaCl_2 , NH_4NO_3 , KH_2PO_4 , KI , and NaBr (0.5 mM each). As shown in Fig. 2, the degree of retention for anions and cations was related to the AECs of the columns in Section 3.2.

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