

Short communication

High-speed ion-exclusion chromatography of dissolved carbon dioxide on a small weakly acidic cation-exchange resin column with ion-exchange enhancement columns of conductivity detection

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Abstract

The high-speed ion-exclusion chromatographic determination of dissolved carbon dioxide, i.e., carbonic acid, hydrogencarbonate or carbonate, with conductivity detection was obtained using a small column packed with a weakly acidic cation-exchange resin in the H⁺-form (40 mm long × 4.6 mm i.d., 3 μm-particle and 0.1 meq./ml-capacity). Two different ion-exchange resin columns, which were a strongly acidic cation-exchange resin in the K⁺-form and a strongly basic anion-exchange resin in the OH⁻-form, were connected after the separation column. The sequence of columns could convert dissolved carbon dioxide to KOH having high conductivity response. The enhancement effect for dissolved carbon dioxide could retain even on the vast chromatographic runs, by using the enhancement columns with high ion-exchange capacity above 1.0 meq./ml. The retention time was in 60 s at flow-rate of 1.2 ml/min. The calibration graph of dissolved carbon dioxide estimated as H₂CO₃⁻ was linear in the range of 0.005–10 mM. The detection limit at signal to noise of 3 was 0.15 μM as H₂CO₃⁻. This method was applicable to several rainwater and tap water samples.

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1. Introduction

Recently, high-speed ion chromatographic separations that can separate analyte samples in sub-minutes or a few minutes have been very efficient for the increased sample throughput and productivity [1–3]. While the improvements of separation speed in ion chromatography have been advanced, those in ion-exclusion chromatography have been inactive. This seems to be due to the limited applicability to analyte samples compared with ion chromatography. However, the technique has been suitable for the determination of aliphatic carboxylic acids, weak inor-

ganic acids and sugars in environmental, food or agricultural water samples [4–9]. Especially, the ion-exclusion chromatography of dissolved carbon dioxide, i.e., hydrogencarbonate, carbonate or carbonic acid, can simply obtain using a column packed with a cation-exchange resin in the H⁺-form with water eluent [7,8]. Unfortunately, the analytical problem is to lead to a fronted peak, as well as the long analysis time (ca. 5–15 min).

The purpose of this study is to achieve the high-speed ion-exclusion chromatography of dissolved carbon dioxide, minimizing the fronted peak. The separation column in this study is a small column (40 mm × 4.6 mm i.d.) packed with a polymethacrylate-based weakly acidic cation-exchange resin in the H⁺-form with 3 μm-particles and 0.1 meq./ml-capacity [10]. The cation-exchange capacity of this column is smaller than that used in the previous study (0.2 meq./ml) [10], in order to increase

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the penetration effect of dissolved carbon dioxide to the resin phase.

The other problems are to be the low conductimetric sensitivity due to the low limiting equivalent ionic conductance of dissolved carbon dioxide, and the narrow concentration ranges of calibration linearity due to the incomplete ionization of high concentration of dissolved carbon dioxide. The several methods in order to improve the detector response were reported, e.g., two-dimensional conductivity detection system with ion-exchange enhancement by Dasgupta and co-worker [11], or indirect UV detection by Voloshik et al. [12]. Here, the method developed by Tanaka and Fritz [8] was adopted, which convert dissolved carbon dioxide into a highly ionized compound (KOH) by two different ion-exchange resin columns connected after the separation column. This can easily enhance the conductivity response of dissolved carbon dioxide by the three columns connected in the tandem line. The ion-exchange columns packed with the high ion-exchange capacity (>1.0 meq./ml) was used in order to maintain the conductimetric enhancement effect for the vast chromatographic runs without the regenerations.

We report for: (1) the high-speed ion-exclusion chromatography of dissolved carbon dioxide by the small separation column; (2) the expansion for the calibration linearity by connecting the ion-exchange enhancement columns and the durability; and (3) its application to the several real water samples.

2. Experimental

The ion chromatograph was Tosoh IC-2001 consisted of a dual pump, an on-line degasser, a column oven operated at 40°C , a conductimetric detector and an automatic sample injector. The data analysis is Tosoh IC-WS version 3. Flow rate was 1.2 ml/min. Injection volume was 30 μl .

All reagents were of analytical reagent-grade, purchased from Wako (Osaka, Japan) and were dissolved in distilled and deionized water for the preparation of standard solutions and eluents. The stock solutions used in this study were prepared by dissolving 0.1 M with distilled and deionized water. Appropriate amounts of analytes at the concentration of 0.1 M each were diluted with water as necessary. Rainwater sample were collected at Seto (Aichi prefecture, Japan), and river water sample were at Seto River (Aichi, Japan). They were injected to the separating column after filtration through a 0.20 μm membrane filter.

A TSKgel Super IC-A/C in the H^+ -form (column 1) with 3 μm -particles and 0.1 meq./ml-capacity (40 mm \times 4.6 mm i.d.) was used as a separation column. A TSKgel OApak-P in the K^+ -form (column 2: polystyrene-divinylbenzene, 5 μm -particles and 1.5 meq./ml-capacity) (50 mm \times 4.6 mm i.d.) was use as a first enhancement column. A TSKgel SAX in the OH^- -form (column 3: polystyrene-divinylbenzene, with 5 μm -particles and 1.0 meq./ml-capacity) (40 mm \times 4.6 mm i.d.) was used as a second enhancement column. In order to trap dissolved carbon dioxide in water eluent, a strongly basic anion-exchange resin in the OH^- -form, TSKgel SAX (40 mm \times 4 mm i.d.) was inserted between elution pump and sample injector [8]. All columns packed specially by Tosoh Co., Ltd. (Tokyo, Japan) were equi-

librated with water eluent for 30 min before chromatographic runs.

3. Results and discussion

3.1. High-speed ion-exclusion chromatography of carbonic acid

A mixture of Na_2SO_4 , NaCl and NaHCO_3 (1 mM for each) was injected to the small separation column in the H^+ -form (column 1) with water as eluent. These analyte samples are converted to sulfuric acid, hydrochloric acid and carbonic acids by passing through the column. The separation of dissolved carbon dioxide from strong acids could be obtained in 40 s at 1.2 ml/min, as shown in Fig. 1A. The peak shape by column 1 was much better than that by 15 cm long column with the same particles and capacity as column 1. The fronted peak is often obtained from ion-exclusion chromatography with water, because the degrees of ionizations of analytes are changed moving through the column and the ionized portion of sample is eluted faster. The degrees of fronted peak shape are dependent on the dimension of column from these results. Unfortunately, the conductivity response of dissolved carbon dioxide was low due to its limiting equivalent ionic conductance (44.5 Scm^2/mol as HCO_3^-). The linearity of calibration graph was ranged from 0.025 to 1.0 mM.

3.2. Effect of two ion-exchange enhancement columns

A strongly acidic cation-exchange resin column in the K^+ -form as the first enhancement column was used to obtain a more sensitive conductivity detection of carbonic acid. When this column is inserted between the separation column and the detector, carbonic acid as partially ionized form is converted to KHCO_3 of highly ionized form.

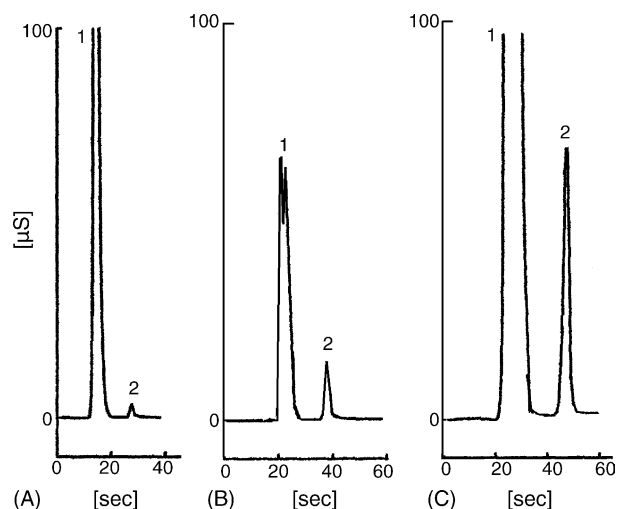


Fig. 1. Comparison of ion-exclusion chromatograms of dissolved carbon dioxide with and without first and second enhancement columns; Sequence of columns: (A) column 1; (B) columns 1 + 2; and (C) columns 1 + 2 + 3. Sample: a mixture of Na_2SO_4 , NaCl and NaHCO_3 (1 mM for each). Injection volume: 30 μl . Column temperature: 40°C . Peaks: 1 = SO_4^{2-} and Cl^- , and 2 = HCO_3^- .

In this study, a strongly acidic cation-exchange resin columns in the K^+ -form with 1.5 meq./ml cation-exchange capacity (column 2) was used and tested as the first enhancement column in terms of the enhancement effect of dissolved carbon dioxide with conductivity and the durability in 100-repeated chromatographic runs. With the first enhancement column, the peak height of 1.0 mM HCO_3^- was ca. three-times greater than that without it. The enhancement effect using column 2 was very stable after the 100 runs. The peak of strong acids (H_2SO_4 and HCl) was greatly decreased by converting to K_2SO_4 and KCl passing through the first enhancement column as shown in Fig. 1B. This was because each limiting equivalent ionic conductance of K_2SO_4 (153.5 Scm^2/mol) and KCl (149.9 Scm^2/mol) was lower than that of H_2SO_4 (429.8 Scm^2/mol) and HCl (426.2 Scm^2/mol).

In order to obtain the further conductivity response of dissolved carbon dioxide, a strongly basic anion-exchange resin column in the OH^- -form was inserted between the first enhancement column and the detector. The second enhancement column can convert $KHCO_3$ into KOH having the much higher limiting equivalent ionic conductance (KOH : 272.1 Scm^2/mol). Here, a TSKgel-SAX in the OH^- -form with 1.0 meq./ml anion-exchange capacity (column 3) was tested as the second enhancement column. Fig. 1C shows the chromatogram with the enhancement columns 2 and 3. The sharpened peak of dissolved carbon dioxide converted as KOH could be detected in 60 s at 1.2 ml/min. The conductivity response by three-column system was 13.2-times in peak height and 20.0-times in peak area greater than those in the separation column alone.

3.3. Interference of other acids

Fig. 2 shows the ion-exclusion chromatogram of sulfuric, phosphoric, hydrofluoric, acetic, propionic, butyric and dissolved carbon dioxide in order to investigate the interference of dissolved carbon dioxide detected in this system. The strong acids and hydrofluoric acid did not interfere for the dissolved carbon dioxide peak, which later eluted, because they were passed rapidly through this column system. No interference was observed from equal-concentration of formic and acetic acids. Similarly, divalent and trivalent carboxylic acids such as oxalic, tartaric and citric acid were detected before the dissolved carbon dioxide peak (not shown data). However, the peaks of propionic and butyric acids were overlapped with the dissolved carbon dioxide peak and thus interfered. This method was unsuitable for the water samples with organic acids such as propionic or butyric acids.

3.4. Analytical performances

The peak areas of dissolved carbon dioxide (as HCO_3^-) were plotted against various concentrations injected to the three-column system. The calibration curve obtained was linear in the concentration range of 0.005–10.0 mM ($r^2 = 0.9992$), which could expand rather than previous study (0.05–8.20 mM) [7]. The detection limit at signal to noise of 3 was 0.15 μM . The relative standard deviations in the 6th repeated chromatographic runs respectively by injecting 0.005, 0.5, and 5 mM of $NaHCO_3$

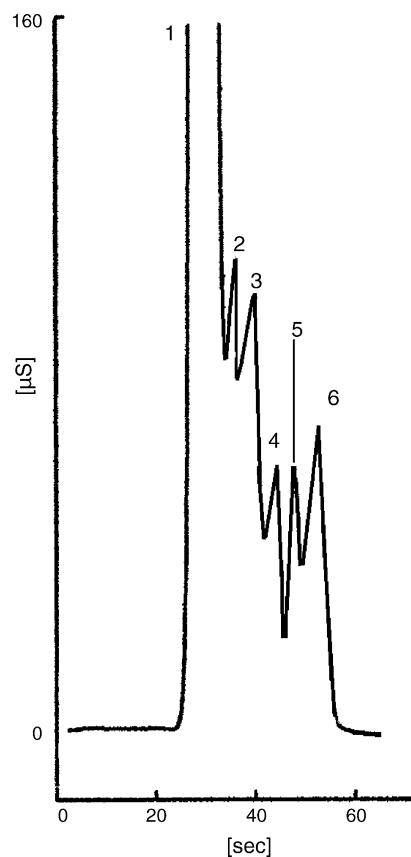


Fig. 2. Ion-exclusion chromatograms of several acids with the first and second enhancement columns; Sequence of columns: columns 1 + 2 + 3. Sample: a mixture of Na_2SO_4 , $NaCl$, NaF , $HCOOH$, CH_3COOH , C_2H_5COOH , C_3H_7COOH , $NaHCO_3$ (1 mM for each). Peaks: 1 = SO_4^{2-} , Cl^- , and F^- , 2 = $HCOO^-$, 3 = CH_3COO^- , 4 = $C_2H_5COO^-$, 5 = HCO_3^- , and 6 = $C_3H_7COO^-$. Other conditions as in Fig. 1.

were pretty good as 0.15–0.92% in peak area and 0.08–0.15% in retention time.

3.5. Application to rain and river water samples

The three-column system was applied to the determination of dissolved carbon dioxide in rainwater and river water samples. Fig. 3 shows the typical chromatograms of dissolved carbon dioxide in the water samples without any dilutions. Successful determination of dissolved carbon dioxide that is present as carbonic acid at pH 4.21 could be obtained using this system for the low sensitive analytes due to the suppressed ionization. In contrast, dissolved carbon dioxide that is present as hydrogen-carbonate in river water at pH 7.21 could be easily determined, when it is no interfered by propionic or butyric acid. The recoveries, when adding 0.005 mM $NaHCO_3$ in the rainwater and 0.05 mM $NaHCO_3$ in the river water, were 96% in the rainwater and 97.2% in the river water.

In concluding, the high-speed determination of dissolved carbon dioxide in 60 s could be obtained using the combination of the small three different ion-exchange columns. As final points, the overall sample turn-around time (washing of syringe,

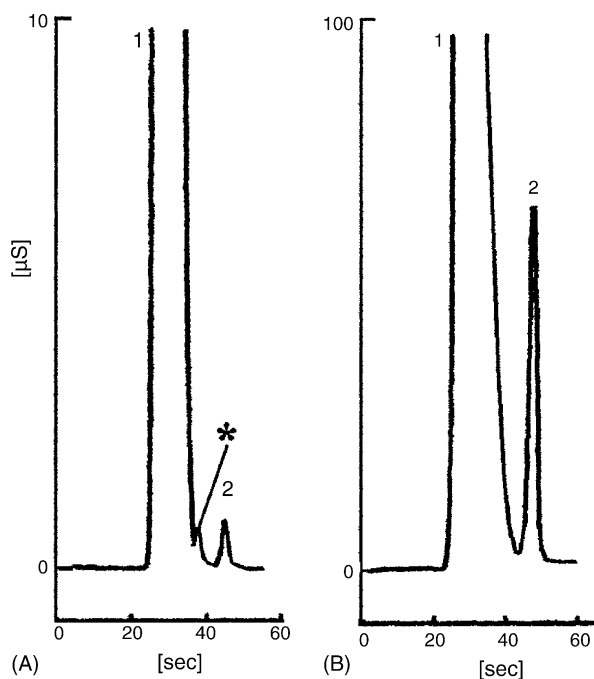


Fig. 3. Ion-exclusion chromatograms of dissolved carbon dioxide in rainwater and river water samples; Sequence of columns: columns 1 + 2 + 3. Samples (pH): (A) rainwater (pH 4.21); and (B) river water (pH 7.21). Peaks: 1 = strong acid anions; 2 = HCO_3^- ; and * = unknown peaks. Other conditions as in Fig. 1.

injection of sample and separation) in this method was in 3 min, and thus 20 runs in 1 h were possible. Further investigations must consider the problems for the practical application of ion-exclusion chromatography in the real sample water.

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