

Dodecylsulfate-coated monolithic octadecyl-bonded silica stationary phase for high-speed separation of hydrogen, magnesium and calcium in rainwater

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Received 1 April 2003; received in revised form 10 October 2003; accepted 11 November 2003

Abstract

The high-speed determination of hydrogen, magnesium and calcium ions by ion chromatography (IC) is demonstrated on a monolithic octadecyl-bonded silica (ODS) column coated with lithium dodecylsulfate (Li-DS). This stationary phase, when used in conjunction with a 2 mM ethylenediamine and 0.1 mM Li-DS solution as eluent at pH 6.0, was found to be suitable for the rapid and efficient separation of hydrogen and magnesium and calcium in the order $H^+ < Mg^{2+} < Ca^{2+}$ within 4 min at a flow rate of 4.0 ml/min. Under the conditions, linear calibration plots of conductivity versus concentration were obtained for the cations over about three orders of magnitude, and the detection limits were 1 μ M for H^+ , 2 μ M for Mg^{2+} and Ca^{2+} . Rainwater was analyzed directly using this IC system with satisfactory results.

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Keywords: Rainwater; Stationary phases, LC; Monolithic columns; Hydrogen; Magnesium; Calcium; Ethylenediamine; Inorganic cations; Lithium dodecylsulfate

1. Introduction

Recently some researchers tried to use ion chromatography (IC) to determine hydrogen ion (H^+) to be as a supplement for the two frequently used methods, acid–base titration and potentiometry [1–4]. DeBorba et al. [5] demonstrated the ability of sulfonated styrenedivinylbenzene stationary phases to separate H^+ from other monovalent cations (Li^+ , Na^+ , NH_4^+ and K^+) using a dilute solution of a neutral salt as eluent; Hu et al. [6,7] separated H^+ and other monovalent cations on an octadecyl-bonded silica (ODS) column coated with dodecylsulfate using acidified solutions of LiCl and EDTA-2K as eluents; the same authors [8] separated H^+ and divalent cations Ba^{2+} , Mg^{2+} and Ca^{2+} on a ODS stationary phase coated with *n*-hexadecylphosphocholine using water as eluent within about 30 min, which detracted from

its usefulness. Therefore, high-speed liquid chromatography (LC) should be tested as an alternative, since run times will be shortened, while chromatographic efficiency and resolution are maintained [9–13]. One useful material for high-speed analysis in LC is monolithic materials [14], which have been successfully applied to bio-separation [15–20], and the analysis of organic homologues analysis [21], common inorganic anions [22] and cations [23,24]. In this study, what we were interested in was its application to the analysis of H^+ , Mg^{2+} and Ca^{2+} , the important ionic components in acid rain. A monolithic-type column was modified by saturating it with lithium dodecylsulfate (Li-DS), on which the three cations were separated well within 4 min when an acidified ethylenediamine solution containing small concentration of dodecylsulfate was used as eluent at a flow-rate of 4 ml/min; however, under the specified conditions the alkali metal and ammonium ions co-eluted due to their weak retention on the stationary phase and strong elution ability of ethylenediamine [1].

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2. Experimental

2.1. Chemicals and sample preparation

All reagents were of analytical reagent-grade, purchased from Wako (Osaka, Japan) and were dissolved in deionized water ($\geq 18 \text{ M}\Omega \text{ cm}$). Stock standard solutions of cations were prepared by dissolving appropriate amounts of hydrochloric acid, potassium chloride, sodium nitrate, ammonium chloride, calcium chloride and magnesium sulfate in water at a concentration of 0.1 M. These were diluted as necessary (using boiled deionized water stored in a closed container to prepare the standard solutions with different pH values). Hydrochloric acid solution was used for adjusting the pH value of eluent. Ethylenediamine was used as component of the eluent. Lithium dodecylsulfate was used for coating the monolithic column.

Quality control procedures [25] were employed in rainwater sample collection. Three replicate samples were collected with volume of about 20 ml and the pH value of each sample first was measured using a pH meter (HM-14P pH meter, TOA Electronics, Tokyo, Japan), and then the samples were filtered through a 0.3 μm nylon-66 membrane filter prior to direct analysis.

2.2. Instrumentation

Experiments were carried out on a Tosoh HPLC System (Tokyo, Japan) consisting a data processing system, a DP-8020 eluent delivery pump, a CM-8020 conductimetric detector, a CO-8020 column oven, an SD-8022 degasser and an SIL-6B injector equipped with a 100 μl sample loop. The rainwater samples were analyzed on a Chromolith column (5.0 cm \times 4.6 mm i.d., Merck, Germany) modified by passing about 50 ml of 40 mM Li-DS solution through the column at a flow-rate of 0.5 ml/min under the followed chromatographic conditions: the eluent was composed of 2 mM ethylenediamine and 0.1 mM Li-DS (pH 6.0) at a flow-rate of 4.0 ml/min; the gain of conductimetric detector was 0.1 $\mu\text{S}/\text{cm}$, the response was FAST (response time 0.1 s) and the polarity was negative; the column temperature was kept at 35 $^{\circ}\text{C}$; and the instrument was equilibrated for about 30 min prior to use.

3. Results and discussion

3.1. Cation retention on dodecylsulfate-coated stationary phase using ethylenediamine solution as eluent

Dynamic coating of ODS materials with anionic surfactant dodecylsulfate (DS) is a well-established and convenient means to create a stationary phase for separating cations. When using an ethylenediamine (En) solution with pH 6.0 (at which the most predominant existing sort of ethylenediamine is divalent cations, EnH_2^{2+} [26]) as eluent, the sep-

aration of H^+ , Mg^{2+} and Ca^{2+} on the DS-coated stationary phase was performed by cation-exchange, as evidenced by calculating the slopes regression factors (R^2) of plots of $\log [\text{EnH}_2^{2+}]$ against $\log k'$ of H^+ , Mg^{2+} and Ca^{2+} . Here, $[\text{EnH}_2^{2+}]$ denotes the molar concentration of EnH_2^{2+} in the eluent and k' is the retention factor of the cations. The results showed that all R^2 values exceeded 0.9994 and slopes were -0.4851 for H^+ , -0.9916 for Mg^{2+} and -0.9921 for Ca^{2+} , which demonstrated these cations were separated by cation-exchange.

The elution order of common mono- and divalent cations was $\text{Li}^+ \approx \text{Na}^+ \approx \text{NH}_4^+ \approx \text{K}^+ < \text{H}^+ < \text{Mg}^{2+} < \text{Ca}^{2+}$. The co-elution of alkali metal and ammonium ions was due to their weak retention and the strong elution ability of ethylenediamine [1]; the separation of H^+ from other monovalent cations was attributed to the protonated DS-coated stationary phase resulting in stronger retention of H^+ [27].

3.2. Effect of eluent

Experiments showed that with increasing the concentration of ethylenediamine in the eluent, the retention time of H^+ , Mg^{2+} and Ca^{2+} decreased and the background conductivity increased. When the concentration exceeded 2 mM, the H^+ peak was not separated adequately from the peak of other monovalent cations and high background conductance decreased the detection sensitivity. Therefore, 2 mM ethylenediamine was chosen as a compromise.

Maintaining a certain concentration of Li-DS in the eluent was to replace the lost dodecylsulfate on the stationary phase. Investigations on the changes in peak area with increasing Li-DS concentration showed that peak areas remained almost unchanged when Li-DS concentration increased over the range of 0.08–0.2 mM. The test of life-span of the monolithic DS-coated stationary phase showed that when the Li-DS concentration was 0.1 mM, the surfactant-coated stationary phase was found to be stable during at least 1 month (operated daily for about 6 h) with the relative standard deviations (R.S.D.) for retention times, peak area and peak height all being less than 4.7%. Therefore, 0.1 mM Li-DS in the eluent was selected.

Extreme eluent pH values of cause were avoided because H^+ was the target ion. The effect of eluent pH value from pH 3.0 to 6.5 on peak area was investigated. As shown in Fig. 1, H^+ peak area increased significantly from pH 3.8, and was up to the biggest and changed slightly between pH 5.8 and 6.5; for Mg^{2+} and Ca^{2+} ions, the responses both decreased from pH 3.0, and remained small changes over the eluent pH range of 4.0–6.0. An eluent pH of 6.0 was selected, at which satisfactory responses of the cations were obtained.

Fig. 2 shows the changes in theoretical plates of the three cations on the DS-coated monolithic column at different flow-rates, using N_{df} as the measure of efficiency, calculated according to the Dorsey–Foley equation, which is for calculating the column efficiency of the surfactant-coated monolithic columns [28]. As shown in Fig. 2, the theoret-

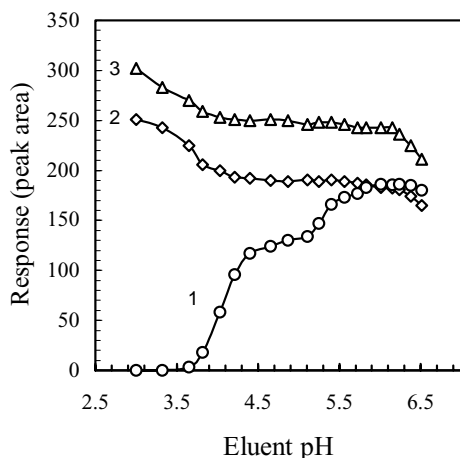


Fig. 1. Changes in responses (peak area) of target ions with different eluent pH value on the DS-coated monolithic stationary phase (Merck Chromolith column, 5.0 cm \times 4.6 mm i.d.). Eluent, 2 mM ethylenediamine solution with pH 6.0 containing 0.1 mM Li-DS; sample, a standard solution mixture of 0.10 mM H^+ , Mg^{2+} and Ca^{2+} ; 1 = H^+ , 2 = Ca^{2+} , and 3 = Mg^{2+} ; column temperature, 35 $^{\circ}\text{C}$; flow-rate, 4.0 ml/min; injection volume: 100 μl .

ical plates of the three cations were relative constant over the flow-rate range of 2.5–4.0 ml/min, which demonstrated the merits of using monolithic column at a high flow-rate. Here, 4.0 ml/min was therefore selected.

3.3. Analysis performance

Analyses were carried out under the optimized chromatographic conditions and reproducibility was estimated by making replicate injections ($n = 5$) of a spiked rainwater sample. The relative standard deviations (R.S.D.) of peak area of the cations were all $< 1.7\%$. The column-to-column reproducibility of the surfactant-coated column was esti-

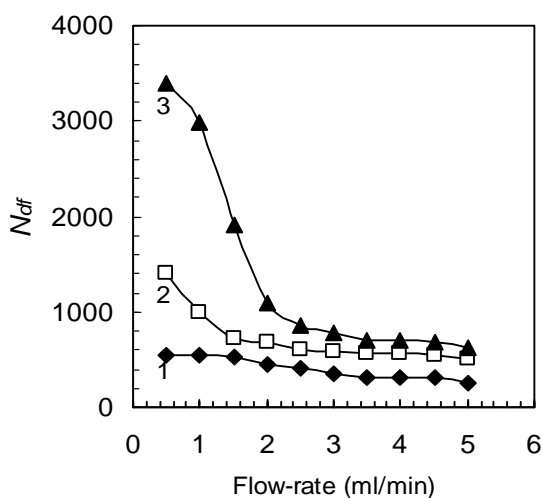


Fig. 2. Changes in the number of plate (N_{df}) on the DS-coated monolithic column at different flow-rate. 1 = H^+ , 2 = Mg^{2+} and 3 = Ca^{2+} ; others as in Fig. 1.

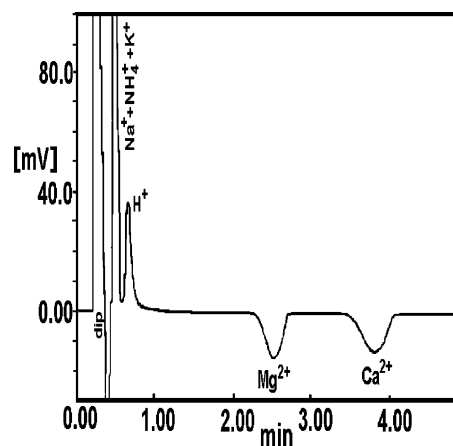


Fig. 3. Chromatogram of a spiked rainwater sample (mixture of rainwater sample and a standard solution containing 0.30 mM H^+ , Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+} , respectively) on the DS-coated monolithic stationary phase (Merck Chromolith column, 50 mm \times 4.6 mm i.d.). Column temperature, 35 $^{\circ}\text{C}$; eluent, 2 mM ethylenediamine solution containing 0.1 mM Li-DS (pH 6.0); flow-rate, 4.0 ml/min; injection volume: 100 μl .

Table 1

Analysis of three rainwater samples by the proposed IC and conventional methods ($n = 3$)

Ion	Sample 1 (μM)		Sample 2 (μM)		Sample 3 (μM)	
	This IC	Other	This IC	Other	This IC	Other
H^+	19.4	19.0 ^a	25.8	24.9 ^a	18.7	19.0 ^a
Mg^{2+}	16.3	15.9 ^b	17.9	17.6 ^b	27.5	28.3 ^b
Ca^{2+}	20.5	21.3 ^b	24.3	23.7 ^b	21.6	22.5 ^b

^a H^+ : a potentiometric pH meter.

^b Mg^{2+} and Ca^{2+} : conventional cation-exchange IC.

ated by coating the column three times and injecting a mixture of cations five times. The R.S.D. of peak area of the cations were all $< 1.4\%$. Calibration linearity for conductivity detection of H^+ , Mg^{2+} and Ca^{2+} was found to extend over the range 10 μM to 2.5 mM (pH 2.6–5.0) for H^+ and both 5 μM to 1.0 mM for Mg^{2+} and Ca^{2+} . The correlations coefficient was better than 0.9989 for each plot and the detection limits calculated by using 3σ were 1 μM for H^+ , 2 μM for Mg^{2+} and Ca^{2+} (σ , standard deviation of a blank solution; $n = 7$).

Fig. 3 shows the chromatogram of a spiked rainwater sample. The analytic recoveries obtained when analyzing such a sample were 98% for H^+ , 98% for Mg^{2+} and 96% for Ca^{2+} ($n = 7$). Table 1 compares the data obtained with this method with those using a potentiometric pH-meter or a traditional IC method [1]. Good agreement was obtained between them.

4. Conclusions

This work described an IC system for efficiently determining H^+ , Mg^{2+} and Ca^{2+} on a monolithic stationary

phase coated with anionic surfactant. The approach resulted in a separation in real water samples within 4 min with low μM -level detection limits. Future work will be focused on achieving the simultaneous separation of H^+ , Mg^{2+} and Ca^{2+} ions as well as monovalent cations such as Na^+ , NH_4^+ and K^+ .

Acknowledgements

The authors were grateful to the Japan Society for the Promotion of Science (JSPS), for the award of a postdoctoral fellowship (PB01097) and financial support. They also would like to thank Ms. Yukiko Kamata for her enthusiastic assistance.

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