

Monolithic octadecylsilyl-silica gel column for the high-speed ion chromatographic determination of acidity

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Abstract

A monolithic ODS-silica gel column modified by saturating it with lithium dodecylsulfate (Li-DS) was used to demonstrate the high-speed separation of H^+ from other mono- and divalent cations, such as Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} using ion chromatography (IC). Using a 5 mM EDTA-2K solution containing 0.10 mM Li-DS (pH 4.80) as eluent, H^+ was eluted with a sharp and symmetrical peak within 1.0 min before other cations at a flow-rate of 1.5 ml min^{-1} . The rapid elution of H^+ and its conductimetric detection could be attributed to the presence of EDTA (HY^{2-}), which can convert H^+ ions as anions, i.e. $H^+ + H_2Y^{2-} \rightarrow H_3Y^-$. The acidity of rainwater and deionized water samples was determined using this IC system with satisfactory results.

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1. Introduction

Recently, some studies have been carried out in the field of high-speed separation by liquid chromatography (LC). Advantages are not only being gained from reduced chromatographic run times but also by maintaining chromatographic efficiency and resolution. Within the field of LC, most attention has been focused on the reversed-phase separations of pharmaceuticals [1], biomolecules [2] and environmental contaminants [3]. This kind of LC method has also been applied to the field of ion chromatography (IC). Connolly and Paull [4] separated nine

common inorganic anions within 160 s on a short octadecylsilyl (ODS)-silica column permanently coated with didodecyltrimethylammonium bromide. Hu et al. [5] used an electrostatic ion chromatography method to achieve rapid and direct determination of iodide in seawater using an ODS column modified by coating it with Zwittergent-3-14 micelles.

Monolithic materials have become useful stationary materials for high-speed analysis in HPLC [6]. The preparation of monolithic columns is usually based on a sol-gel process for the preparation of monolithic porous silica rods using highly pure metal-free alkoxysilanes. The silica rod possesses a biporous structure typically consisting of macropores and mesopores in the skeleton providing a high porosity compared with particulate columns. There-

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fore, this kind of column can be operated at higher flow-rates without much loss of performance and limitations due to column backpressure. The monolithic materials have already been applied successfully to bioseparations [7–12], organic homologue analysis [13] and common inorganic anion separation [14] by HPLC. In this study, what we were interested in was its application to high-speed separation of hydrogen ions (H^+) to overcome some of the remaining limitations of the IC methods projected for H^+ determination.

Some researchers have tried to use the IC method to overcome the disadvantages, such as low detection limit, low sensitivity and/or complicated operating steps, of the two frequently used methods, acid–base titration and potentiometry [15–17], and others methods, i.e. NMR (nuclear magnetic resonance) [18,19] and spectrophotometry [20,21] for the determination of H^+ . De Borba et al. [22] demonstrated the ability of sulfonated styrene–divinylbenzene stationary phases to separate H^+ from other cations using a dilute solution of a neutral salt as eluent. The method was highly sensitive to small changes in H^+ concentration; however, its ultimate H^+ detection limit was down to the low mM level. Hu et al. [23–26] developed the ion chromatographic method for determining H^+ . They used an ODS column modified with dodecylsulfate as stationary phase and acidified LiCl [24] and EDTA-2K [25] solutions as eluents to determine H^+ directly down to μM levels. Although the detection limits have been significantly improved, the retention times of H^+ , as have been reported, were over 10 and 4 min, respectively, which demonstrated the inadequacy for actual applications.

In this work, the aim was to establish an effective IC system to determine H^+ with characteristics of being rapid, sensitive and practical. A monolithic ODS-silica gel column has first been used for the high-speed ion chromatographic determination of acidity of real water samples. This monolithic-type column was modified with lithium dodecylsulfate (Li-DS), where H^+ could be eluted with a sharp and highly symmetrical peak within 1 min using an acidified solution containing EDTA-2K and Li-DS as eluent. Compared to the previously reported IC methods, the merits of this method are high-speed analysis (retention time less than 1 min), lower

detection limit ($0.372 \mu M$) and wider linear range (from 10.0 mM to $0.955 \mu M$).

2. Experimental

2.1. Reagents

All reagents were of analytical reagent-grade, purchased from Wako (Osaka, Japan) and were dissolved in deionized water ($0.48 \mu S \text{ cm}^{-1}$) for the preparation of standard solutions and eluents. 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 at a concentration of 0.10 mol l^{-1} . They were diluted as necessary (using boiled deionized water stored in a closed container to prepare standard solutions with different pH values). Lithium hydroxide solution was used for adjusting the pH value of the eluent. Ethylenediaminetetraacetic acid, dipotassium salt dihydrate (EDTA-2K), and ethylenediaminetetraacetic acid, disodium salt dihydrate (EDTA-2Na) were used as components of the eluent, respectively. Lithium dodecylsulfate (Li-DS) was used for modifying the monolithic column.

2.2. Equipment

All experiments were carried out on a Tosoh HPLC system (Tokyo, Japan) with a data processing system and including a non-metallic eluent delivery pump (DP-8020), a conductimetric detector (CM-8020), a column oven (CO-8020), a degasser (SD-8022) and an injector equipped with a 100- μl sample loop. A HM-14P TOA pH meter (TOA Electronics, Tokyo, Japan) was used for determining pH values of samples.

2.3. Stationary phase preparation

The modification of the Merck Chromolith column ($5 \text{ cm} \times 4.6 \text{ mm I.D.}$, Merck, Darmstadt, Germany) was achieved by passing about 50 ml of a 40 mM Li-DS solution through the column at 0.50 ml min^{-1} flow-rate.

2.4. Chromatographic conditions

The eluent was composed of 5.0 mM EDTA-2K and 100 μ M Li-DS using LiOH solution to adjust the pH value to 4.80. The gain of the conductimetric detector was 0.1 μ S cm^{-1} , the response was STD (response time 1 s) and the polarity was negative. The eluent flow-rate was 1.5 ml min^{-1} . The baseline drift was minimized by keeping the column temperature at 35 $^{\circ}\text{C}$, and the instrument was equilibrated for about 30 min prior to use.

2.5. Sample analysis

Rainwater samples were collected at The National Institute of Advanced Industrial Science and Technology (AIST) at Seto, Aichi, Japan using 1000-ml polyethylene bottles with wide polyethylene funnels. Replicate samples were collected and quality control procedures were employed [27]. All sampling vessels were washed with detergent, soaked with acid and then rinsed thoroughly with deionized water and oven dried at 40 $^{\circ}\text{C}$. The installations were placed on the ground at a height of about 1.2 m. The sampling time was 2 h and sample volume was about 20 ml. Three replicate samples were collected throughout. Then, each sample was poured into a 50-ml polyethylene bottle. After collection, the pH value of each sample was measured using a conventional pH meter, and then the sample was filtered through a 0.30- μ m Nylon-66 membrane filter prior to direct analysis. Deionized water samples were collected in our laboratory. Subsequently, all the samples were analyzed according to the chromatographic conditions specified.

3. Results and discussion

3.1. Retention behavior of cations

Coating a reversed-phase ODS with dodecylsulfate (DS) is a commonly used method to create a sulfonated stationary phase for separating cations in IC based on a cation-exchange mechanism. When an aqueous solution of EDTA-2K is used as eluent, it is the K^{+} ions that bind –DS groups on the stationary phase. Experimental results showed that the plots of

$\log [\text{K}^{+}]$ against $\log k'$ of H^{+} and Na^{+} , respectively were both straight lines with slopes greater than 0.9985, which shows that these cations were separated by cation-exchange. $[\text{K}^{+}]$ denotes the molar concentration of K^{+} in the eluent and k' is the retention factor of the cations.

As for the exceptional elution order of the common mono- and divalent cations ($\text{H}^{+} < \text{Na}^{+} < \text{Ca}^{2+} < \text{Mg}^{2+}$) using EDTA-2K solution as eluent, the reasons were the same as have been discussed by Hu et al. [25]. The presence of EDTA (H_2Y^{2-}) in the eluent could accelerate the elution of H^{+} as the anionic form (H_3Y^{-}) based on the reaction, $\text{H}_2\text{Y}^{2-} + \text{H}^{+} \rightleftharpoons \text{H}_3\text{Y}^{-}$; and form a more stable complex with Ca^{2+} .

3.2. Selection of eluent

H^{+} was the species of analytical interest, which could be retained by dodecylsulfate (DS) on the stationary phase by protonation [28]. Therefore, we used monovalent cations, K^{+} and Na^{+} , as the species for cation exchange. Although H^{+} could be well separated using an EDTA-2Na or EDTA-2K solution as eluent, the latter was still selected. Its advantages were: (i) the retention time of H^{+} decreased because the elution power of K^{+} is greater than that of Na^{+} [25]; (ii) the effect of co-exiting cations, NH_4^{+} and K^{+} , could be eliminated completely using EDTA-2K solution as eluent, since the equivalent conductance of NH_4^{+} is almost the same as that of K^{+} (73.55 $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$ for NH_4^{+} and 73.50 $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$ for K^{+}) [29]. When using EDTA-2Na, what could be eliminated was only the effect of Na^{+} .

3.3. Effect of eluent

To optimize the separation and detection, the effects of EDTA-2K concentration, pH value and flow-rate on the retention time and/or peak area of H^{+} were investigated.

Experiments showed that the retention time of H^{+} decreased and background conductivity of the eluent increased with increasing EDTA-2K concentration in the eluent. However, higher background conductivity of eluent decreases the detection sensitivity. There-

fore, 5 mM EDTA-2K was chosen as optimum based on a compromise among the resolution of the test cation achieved, run time and detection sensitivity.

It is necessary to maintain a certain amount of acid in the eluent so that there is a reservoir of H^+ available in the system to re-protonate any silanol group in case H^+ was dissociated and leached them into solution [24]. Because H^+ was the test ion, extremes of pH value of the eluent were avoided. Therefore, the pH value of the eluent was simply varied from pH 3.00 to 6.26 using HCl and concentrated LiOH solutions to adjust the pH value. As shown in Fig. 1, when $pH > 5.22$, the response (peak area) of H^+ decreased significantly; when the eluent pH value was between 4.38 and 5.22, the response changed slightly; and when $pH < 4.21$, the response decreased dramatically. So, the pH value of eluent was chosen as pH 4.80, the central value in the range.

Flow-rate was also important for high-speed chromatographic analysis. Fig. 2 shows the chromatograms of H^+ and Table 1 shows the changes in

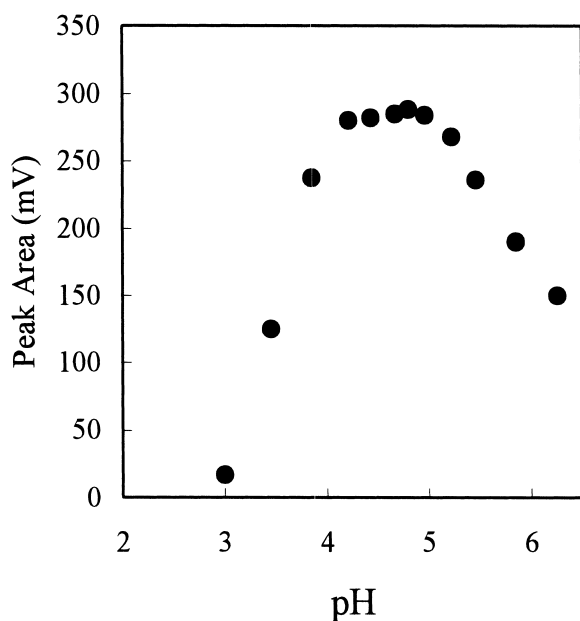


Fig. 1. Effect of pH value of eluent on the response of H^+ ion (peak area). Column, a Merck Chromolith column (5.0 cm \times 4.6 mm); column temperature, 35 °C; Eluent, EDTA-2K–Li-DS (100 μM)–water; flow-rate, 1.5 ml min^{-1} ; sample, 0.100 mM H^+ solution; injection volume: 100 μl .

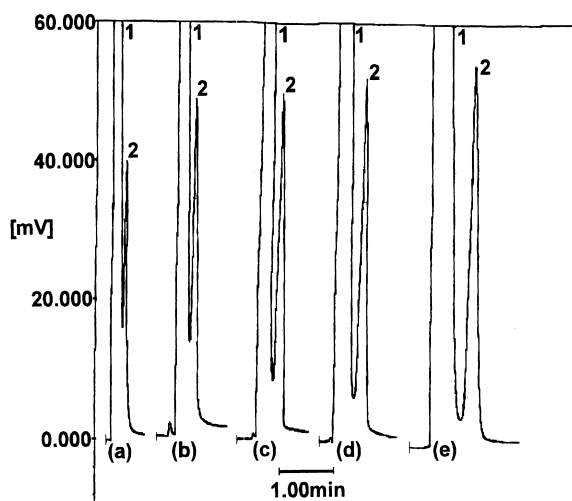


Fig. 2. Chromatograms of H^+ with different flow-rates. 1=dip; 2= H^+ . (a) 3.0 ml min^{-1} , (b) 2.5 ml min^{-1} , (c) 2.0 ml min^{-1} , (d) 1.5 ml min^{-1} , (e) 1.0 ml min^{-1} . Eluent, EDTA-2K (5 mM)–Li-DS (100 μM)–water. Other chromatographic conditions as in Fig. 1.

response of H^+ and eluent dip (peak area) with different flow-rates. We observed that both resolution and response decreased with flow-rate increase. The decrease in resolution could be attributed to high flow-rate. There was not enough time for eluent dip (containing anions and water from the sample) to be eluted completely when the H^+ was eluted. The decrease in response was attributed to the “penetration effect” of Mou et al. [30]. At different flow-rates, the amount of H^+ ions that could come into “the zone of chromatographic peak” was different. The “lost” H^+ ions were eluted together with the eluent dip, because the area of dip peak decreased with increasing flow-rate (shown in Table 1). In this study, the flow-rate was chosen as 1.5 ml min^{-1} ,

Table 1
Changes in responses (peak area) of H^+ ion and eluent dip with different flow-rates

	Flow-rate (ml min^{-1})				
	1.0	1.5	2.0	2.5	3.0
H^+ ion	412	288	221	196	132
Eluent dip	9739	7807	6693	5206	4027

Values are means of five determinations.

which not only separated H^+ rapidly, but also retained high sensitivity of the determination.

3.4. Elimination of co-existing ions

Because H^+ could be eluted first, other mono- and divalent cations did not interfere in the separation. However, in high-speed analysis their effects could

not be neglected. As specified in Section 3.2, we have reported that using EDTA-2K solution as eluent could eliminate the effects of NH_4^+ and K^+ . As for the effects of divalent cations with much longer retention times, Ca^{2+} and Mg^{2+} , they could be eliminated by injecting 100 μ l of 75 mM EDTA-2K solution after elution of H^+ . The elimination result is shown in Fig. 3. Another dip appeared within 2 min

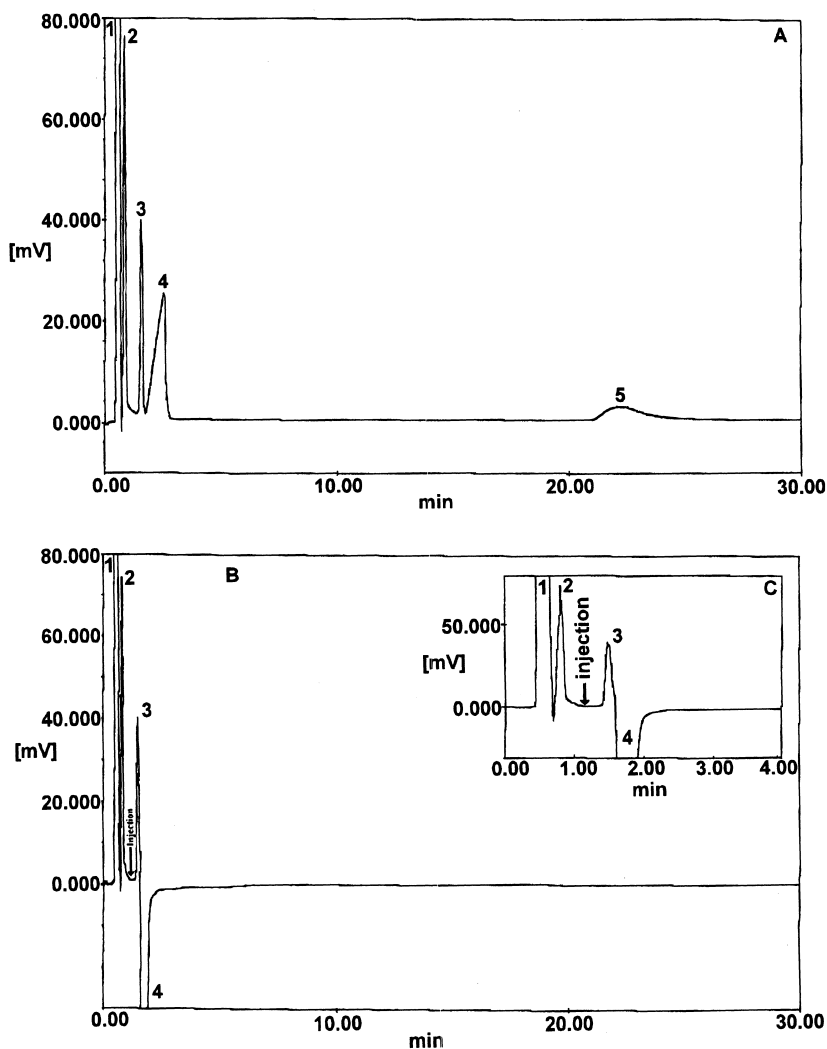


Fig. 3. Chromatograms of (A) injection of a sample solution mixture of 0.08 mM H^+ , Na^+ , Li^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+} . Peaks: 1=eluent dip, 2= H^+ , 3= Li^+ and Na^+ , 4= Ca^{2+} , 5= Mg^{2+} ; (B) injection of 75 mM EDTA-2K solution after elution of H^+ . Peaks: 1=eluent dip 1; 2= H^+ ; 3= Li^+ and Na^+ ; 4=eluent dip 2; and (C) is an enlarged part of (B). Column, a Merck Chromolith column (5.0 cm \times 4.6 mm); column temperature, 35 $^\circ$ C; eluent, EDTA-2K (5.00 mM)–Li-DS (100 μ M)–water with pH 4.80; flow-rate, 1.5 ml min $^{-1}$; injection volume: 100 μ l.

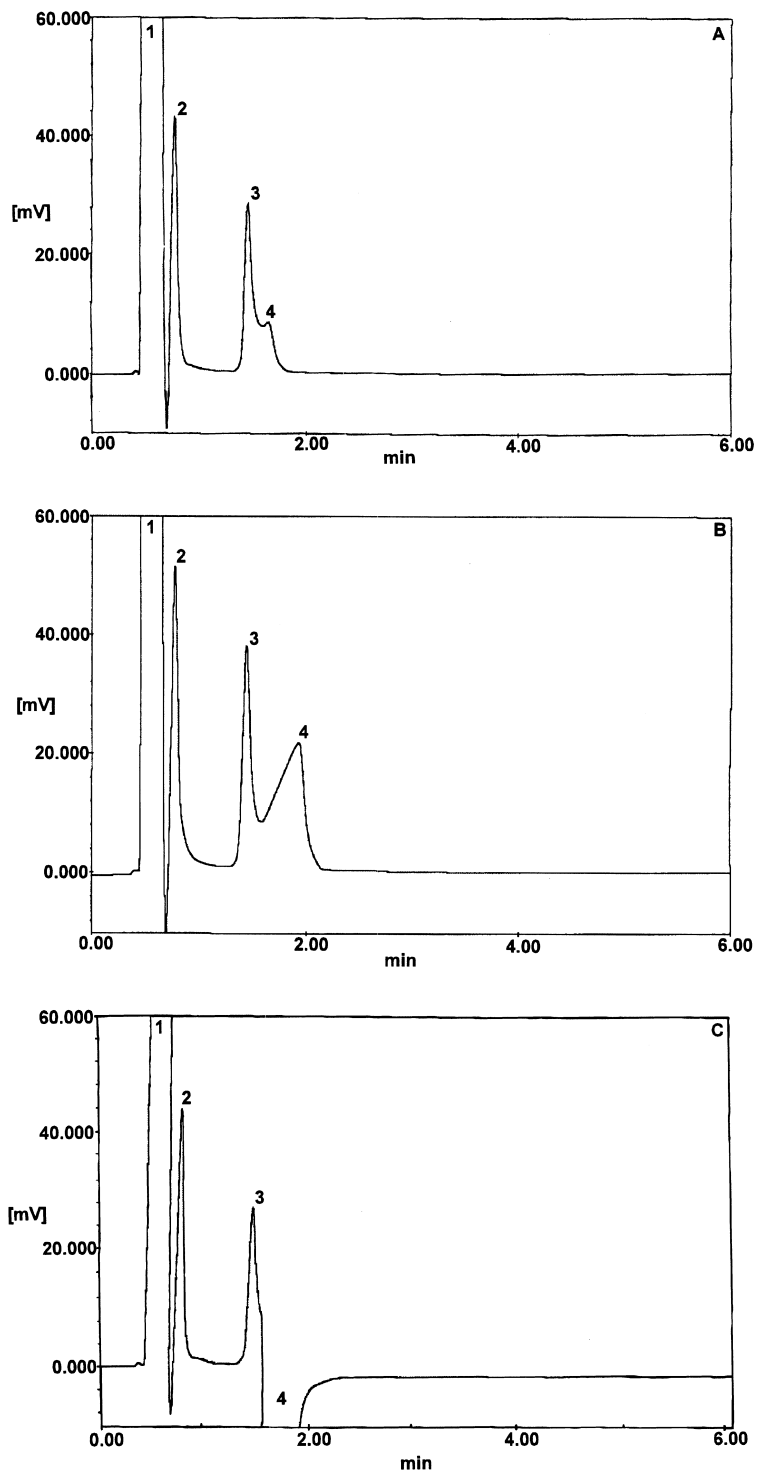


Fig. 4. Chromatograms of (A) rainwater sample, (B) rainwater sample A+standard solution (mixture of 0.075 mM H⁺, Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) and (C) injection of 75 mM EDTA-2K solution after elution of H⁺. Peaks: for (A) and (B), 1=eluent dip; 2=H⁺; 3=Na⁺; 4=Ca²⁺; for (C), 1=eluent dip 1; 2=H⁺; 3=Na⁺; 4=eluent dip 2. Chromatographic conditions as in Fig. 3.

after the injection of EDTA-2K solution. Therefore, the high-speed analysis of H^+ in real water samples containing Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+} ions could be completed within 2 min.

3.5. Reproducibility and stability of the modified column

The reproducibility was estimated by making replicate injections ($n=5$) of a mixture of a rainwater sample and a standard solution containing H^+ , Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+} ions. The relative standard deviation (RSD) of the peak area of H^+ was $<1.34\%$. The column-to-column reproducibility of the modified column was estimated by modifying the column three times and injecting a H^+ standard solution five times. The RSDs of chromatographic peak areas of these cations were $<1.89\%$.

The column modified with Li-DS was stable for at least 2 months of operation with no evidence of peak area/height changes in these cations, which was tested using a $0.10\text{ mM } H^+$ standard solution. The RSDs of these cations were $<1.88\%$.

3.6. Linearity and detection limits

To determine the linearity for H^+ by this method with conductivity detection, a series of standard solutions of H^+ from 30.00 mM to $0.642\text{ }\mu\text{M}$ were tested. The range of linear relationships observed between conductivity and concentrations was from 10.00 mM to $0.955\text{ }\mu\text{M}$ for H^+ . Its correlation coefficient was more than 0.9992 and the detection limit calculated using 3σ was $0.372\text{ }\mu\text{M}$ (σ represents the standard deviation of the blank solution, $n=7$).

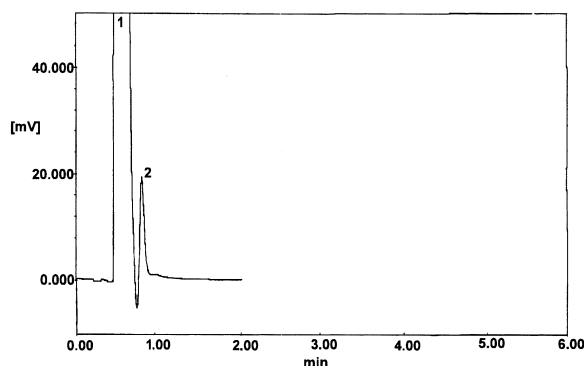


Fig. 5. Chromatograms of deionized water made in our laboratory. Peaks: 1=eluent dip; 2= H^+ . Chromatographic conditions as in Fig. 3.

3.7. Application

This IC method was applied to the determination of acidity of rainwater and deionized water samples. Typical chromatograms of rainwater are shown in Fig. 4, and the chromatogram for deionized water is shown in Fig. 5. The analysis was carried out according to the procedure specified above. The recoveries obtained with this method were tested by analysis of a spiked rainwater sample and replicate injections ($n=7$). Comparing the data for rainwater and deionized water samples determined by this method with that using a potentiometric pH meter, the results were consistent, which demonstrated that this method was reliable for the determination of acidity of real water samples. The results are given in Table 2.

4. Conclusions

This work demonstrates the high-speed determi-

Table 2
Content of H^+ ion in rainwater and deionized water

Sample	Detection by the proposed IC method					Detection by pH meter	
	pH	RSD (%)	Added (μM)	Found (μM)	Recovery (%)	Mean (mM)	RSD (%)
Rainwater	4.716	1.02	100	102	102	4.72	1.96
Deionized water	5.564	1.03	100	97.8	97.8	5.56	2.13

Values are means of seven determinations.

nation of acidity using ion chromatography on a monolithic stationary phase. This approach resulted in a separation of real water samples within 2 min with lower μM levels of detection and a wide linear range (pH 2–6). Future work will be focused on achieving the high-speed and simultaneous chromatographic separation of H^+ together with these mono- and divalent cations.

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References

- [1] K. Heinig, J. Henion, J. Chromatogr. B 732 (1999) 445.
- [2] J.J. Kirkland, F.A. Truszkowski Jr., C.H. Dilks, G.S. Engel, J. Chromatogr. A 890 (2000) 3.
- [3] A.C. Hogenboom, P. Speksnijder, R.J. Vreeken, W.M.A. Niessen, U.A.Th. Brinkman, J. Chromatogr. A 777 (1997) 81.
- [4] D. Connolly, B. Paull, J. Chromatogr. A 953 (2002) 299.
- [5] W. Hu, P.Y. Yang, K. Hasebe, P.R. Haddad, K. Tanaka, J. Chromatogr. A 956 (2002) 103.
- [6] S. Senda, N. Tanaka, Hitachi Sci. Instrum. News 44 (2001) 4022.
- [7] S. Hjerten, J.L. Liao, R. Zhang, J. Chromatogr. 473 (1989) 273.
- [8] S. Hjerten, Y.M. Li, J.L. Liao, J. Mohammad, K. Nakazato, G. Pettersson, Nature 356 (1992) 810.
- [9] Y.M. Li, J.L. Liao, K. Nakazato, J. Mohammad, L. Terenius, S. Hjerten, Anal. Biochem. 233 (1994) 153.
- [10] Ch.M. Zeug, J.L. Liao, K. Nakazato, S. Hjerten, J. Chromatogr. A 753 (1997) 227.
- [11] H. Minakuchi, K. Nakanishi, N. Soga, N. Ishizuka, N. Tanaka, Anal. Chem. 68 (1996) 3498.
- [12] G. Dear, R. Plumb, D. Mallett, Rapid Commun. Mass Spectrom. 15 (2001) 152.
- [13] K. Cabrera, D. Lubda, H.M. Eggenweiler, H. Minakuchi, K. Nakanishi, J. High Resolut. Chromatogr. 23 (2000) 93.
- [14] P. Hatsis, C.A. Lucy, Analyst 127 (2002) 451.
- [15] N.V. Bhagavan, Medical Biochemistry, Jones & Bartlett, London, 1992, p. 16.
- [16] G.D. Christiana, Analytical Chemistry, 15th ed., Wiley, New York, 1994, p. 220.
- [17] X.J. Zhang, B. Ogorevc, J. Wang, Anal. Chim. Acta 452 (2002) 1.
- [18] G.K. Radda, Science 233 (1986) 640.
- [19] S.J.A. Hesse, G.J.G. Ruijter, C.J. Visser Dijkema, J. Biotechnol. 77 (2000) 5.
- [20] G.L. Robert-Baldo, M.J. Morris, R.H. Byrne, Anal. Chem. 57 (1985) 2564.
- [21] I. Lahdesmaki, C. Beeson, G.D. Christiana, J. Ruzicka, Talanta 51 (2000) 497.
- [22] B.M. De Borba, C.M. Kinchin, D. Sherman, T.K. Cook, P.K. Dasgupta, K. Srinivasan, C.A. Pohl, Anal. Chem. 72 (2000) 96.
- [23] W. Hu, K. Hasebe, K. Tanaka, S. Inoue, M. Nagai, Analyst 125 (2000) 2160.
- [24] W. Hu, K. Hasebe, A. Iles, K. Tanaka, Analyst 126 (2001) 821.
- [25] W. Hu, A. Iles, K. Hasebe, H. Matsukami, C.S. Cao, K. Tanaka, Fresenius J. Anal. Chem. 370 (2001) 48.
- [26] W. Hu, K. Hasebe, A. Iles, K. Tanaka, Anal. Sci. 17 (2001) 1041.
- [27] J.S. Cui, Q.Y. Wang, H.P. Han, Monitoring Methods of Atmosphere Pollution, 2nd ed., Chemical Industry Press, Beijing, 1997.
- [28] T. Hirogawa, M. Nishno, N. Aoki, Y. Kiso, J. Chromatogr. 271 (1983) 1.
- [29] M. Oki, T. Osawa, K. Tanaka, H. Chihara, Hand Book of Chemistry, Tokyokagakudojin Press, Tokyo, 1994, p. 1190.
- [30] Y.W. Hou, S.F. Mou, X.P. Hou, F. Liu, S.Y. Tong, Chin. J. Chromatogr. 16 (1998) 347.