Determination of Ammonium and Other Major Cations in River and Rain Water by Ion Chromatography Using Silica Gel as an Ion Exchanger

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The separation of NH₄⁺ from Na⁺, K⁺, Mg²⁺ and Ca²⁺ on silica gel columns was investigated using natural water samples and lithium oxalate as a retention modifier. The pore size of silica gels was found to be the most important factor affecting the retention of the cations. When a 0.0025 mol dm⁻³ lithium oxalate solution of pH 7 was used as the mobile phase these cations could be completely separated on a short silica-gel column (Develosil 30-3, 35 mm×4.0 mm i.d.) within about 20 min. NH₄⁺ contents in river (0.01–0.27 ppm) and rain (1–1.8 ppm) water samples were determined successfully.

Keywords Silica gel column, ion chromatography, sodium, potassium, ammonium, magnesium, calcium, oxalic acid, river water, rain water

Silica gel is known to act as an inorganic ion exchanger.¹ However, the application of silica gel to the chromatographic separation of ionic species is not as popular as those of resin-based ion exchangers.²,³ Recently, Smith and Pietrzyk⁴ have revealed that many inorganic cations are separable on an unmodified silica gel column by ion chromatography (IC). We have also shown some fruitful results regarding the chromatographic separation of alkali and alkaline earth metal cations (M⁺ and M²⁺, respectively) on unmodified silica gel.⁵,⁶ However, nobody has yet succeeded in obtaining a complete separation of NH₄⁺ from K⁺ on silica gel.

We found that silica gel with a small pore size (30 Å, 1 Å=0.1 nm) makes it possible to effectively separate NH₄⁺ from K⁺ on silica gel. This paper describes how NH₄⁺ in river and rain water samples could be successfully determined on a silica gel-oxalate IC system.

Experimental

Reagents

Reagent-grade alkali metal (Merck) and alkaline earth metal chlorides (Wako) were used as received. Deionized water was prepared by the successive use of an Auto Still (WAG-28, Yamato) and an all-quartz-made, non-boiling type distilling apparatus (HF-200, Fujiwara). The test analyte solution was prepared to give concentrations of 0.0025 mol dm⁻³ for M⁺ and 0.01 mol dm⁻³ for M²⁺. The concentrations of M²⁺ were determined by a well-known EDTA titration method. The mobile phase was prepared in the following manner: to a 1-l (1 l=1 dm³) flask, 0.0025 mol of oxalic acid (C₂H₂O₄·2H₂O, Tokyo Kasei) was transferred; about 950 ml of water was added, and then titrated with a concentrated LiOH solution to give pH 7. The resulting solution was adjusted to 1 l in a measuring flask. The mobile phase, thus obtained, was filtered through a membrane filter (pore size: 0.22 µm, Millipore) before use.

Columns

Several types of spherical silica gels (Develosil 30-3, 30-5, 30-7, 60-3, 100-3, Nomura Kagaku) were tested as ion exchangers. The former and latter figures refer to the pore size (Å) and particle size (µm), respectively. The silica gels were made into slurries using a slurry mix (NP type, Chemco) under irradiation of ultrasonic waves and then pumped into stainless-steel columns of different size (35, 50 and 75 mm×4.0 mm i.d.) using a slurry packer (Model 124, Chemco).

Apparatus and procedure

The apparatus used was an assembly of a solvent delivery pump (LC6A, Shimadzu), a syringe-loading sample-injection valve (Model 7125, Rheodyne) equipped with a 200-µl sample loop, a conductivity detector (Model CD-4, Shodex) and an integrator (Chromatocorder 12, System Instruments). An analyte solution of 5 or 10 µl portions was injected by using a 10-µl microsyringe (Hamilton); river-water samples were injected in 200 µl portions through the sample loop. A flow rate of 1.0 ml/min was chosen; the operating
pressures never exceeded 80 kg cm\(^2\). The temperature of the detector was controlled at 25°C in a thermostated air bath.

Na\(^+\), K\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) were also determined with a polarized Zeeman atomic absorption spectrophotometer (Model Z-8000, Hitachi) and NH\(_4^+\) with an ion meter (Model IOC-10, Denki Kagaku Keiki).

**Results and Discussion**

**Chromatograms**

Chromatograms of M\(^+\) and M\(^{2+}\) are depicted separately in Fig. 1. The retention times, t\(_R\), of these cations were increased in the following order:

\[
M^+: Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+
\]

and

\[
M^{2+}: Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}.
\]

The observed sequences were the same as those reported by others.\(^2\)\(^3\) About 15 and 40 min were required for the complete elution of M\(^+\) and M\(^{2+}\), respectively. The peak resolutions were quite satisfactory. The t\(_R\)'s of Rb\(^+\) and Cs\(^+\) were almost the same as those of Mg\(^{2+}\) and Ca\(^{2+}\). Fortunately, naturally occurring water does not contain Rb\(^+\) or Cs\(^+\) to any appreciable extent.

Figure 1 shows that M\(^+\) was observed as positive peaks and M\(^{2+}\) as negative peaks. The reasons why such negative and positive peaks are formed were discussed in detail in our previous papers.\(^6\)\(^7\)

**Pore and particle sizes**

The retention behavior of self-packed columns often differed to a considerable extent from each other. Such was the case with the long columns that have so far been used. Therefore, the effects of the pore and particle sizes on the separation of the analyte cations have not been investigated. The use of a short column (35-mm long), which required little skill to pack, enabled us for the first time to investigate such effects.

In Fig. 2 the dependence of t\(_R\) on the size of the silica gels is shown. A decrease in the pore size remarkably increased t\(_R\) and, as a matter of course, the resolutions of the peaks. The cerificated surface areas of Develosil 30, 60 and 100 are 650, 500 and 350 m\(^2\) g\(^{-1}\), respectively. From these data it is clear that the surface area (the number of ion-exchange sites) governs t\(_R\). Silica gels with a pore size of 30 Å were the most suitable for the separation of analyte cations.

The effect of the particle size was also investigated with three types of silica gels (3, 5 and 7 µm) with the same pore size (30 Å). In these cases, t\(_R\) decreased with decreasing particle size (Fig. 3). This result is inconsistent with that expected from the number of ion-exchange sites. A complete treatment of this subject involves a somewhat detailed study. The silica gels of 3 µm were found to be the most suitable for obtaining well-resolved sharper peaks.

Silica gels with smaller pore size and smaller particle size are suited for the present purpose.
Fig. 3 Effect of particle size on retention time. Silica gel: Develosil 30-3, 30-5 and 30-7; other conditions: see Fig. 2.

**Mobile phase pH**

Different types of weak acids are concerned with the present IC system. Since the degree of dissociation of these acids is governed by the mobile-phase pH, a survey of their dissociation constants is important. The $pK_a$ value of $\text{-Si(OH)}$ is reported to be 7.1 and of $\text{NH}_4^+$ 9.2.9 The $pK_a$ value of $\text{H}_2\text{Ox}$ is 4.28.10 The hydrolysis constants, $pK_{11}$ ($\text{M}^{2+}+\text{H}_2\text{O} \rightleftharpoons \text{M(OH)}^++\text{H}^+$), for $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ are 11.5 and 12.7, respectively.11

From these $pK$ values it can be concluded that alkaline media ranging from pH 7 to 8 are adequate for the present chromatographic purpose since, under such conditions, $\text{-Si(OH)}$ and $\text{H}_2\text{Ox}$ exist as $\text{-SiO}^-$ and $\text{Ox}^{2-}$, respectively. Also any formation of the hydrolyzed cations (e.g., $\text{M(OH)}^{+}$) and of $\text{NH}_3$ can be neglected. Unfortunately, however, it is known that the dissolution of silica gel becomes ever more conspicuous above pH 8. Taking these facts into account, weakly acidic media ranging from pH 5 to 7 were investigated at the cost of a decrease in the number of $\text{-SiO}^-$ sites (a decrease in the ion-exchange capability).

A $t_R$ vs. pH plot is shown in Fig. 4. $t_R$ increased with an increase in the mobile-phase pH; this was due to an increase in the number of $\text{-SiO}^-$ sites. The peak resolution became poorer as the mobile-phase pH decreased. A pH between 6.5 and 7 was satisfactory for a quantitative determination. In view of the detection sensitivity, pH 6.5 was superior to pH 7. At this pH, however, the negative peak of $\text{Mg}^{2+}$ appeared just after the positive peak of $\text{K}^+$. This often resulted in erroneous peak areas due to the lack of a well-defined baseline between both peaks. Hence, a mobile-phase pH of 7 was favored.

**Ligand concentration**

Figure 5 shows the dependence of $t_R$ on the ligand concentration, $C_{ox}$. $t_R$ decreased with an increase in $C_{ox}$. The peak resolutions, however, were very satisfactory, even at $C_{ox}=0.0025 \text{ mol dm}^{-3}$. The use of a concentrated mobile phase significantly shortened the time required for a single run and necessarily increased the height of the peaks. Hence, a 0.0025 mol dm$^{-3}$ oxalate solution was chosen as the mobile phase.

**Column length**

The dependence of the separation of the analyte cations on the column length was investigated. Elution was completed in 15, 20 and 25 min for 35-, 50- and 75-mm columns (4.0 mm i.d.), respectively. The peak
resolutions were quite satisfactory. The preparation of a column shorter than 35 mm was attempted by using commercially available parts; it was unsuccessful because the fittings used at the column ends came into contact. The shortest column was chosen for both rapidity and high sensitivity.

Separation of NH₄⁺ from K⁺

Though from the beginning of our early investigations the complete separation of NH₄⁺ from K⁺ has been an interesting subject, no satisfactory separations have been attained yet. The present investigation was our first success (Fig. 6). However, the complete separation of NH₄⁺ from large quantities of K⁺ still remains unsolved.

Calibration curves

The calibration curves were made under the conditions previously mentioned. Plots of the peak area vs. the analyte concentration (Na⁺ and Ca²⁺; (0 - 10⁻³) mol dm⁻³; K⁺ and Mg²⁺; (0 - 10⁻⁴) mol dm⁻³; NH₄⁺; (0 - 5×10⁻⁵ mol dm⁻³) gave good straight lines with correlation coefficients greater than 0.999. The relative standard deviations for five runs were less than 1%.

Application to river and rain water

Water samples were collected from three major rivers (the Asahi, the Yoshii and the Takahashi rivers) in Okayama prefecture, Japan. The Zasu river (Table 1) originates from the Asahi river and runs through the campus of our university. Tap water also originates from the Asahi river. Four samples were collected at bridges of the Asahi river (from the upper to lower: Katuragi, Nakahara, Shin-Tsurumi and Tsukimi bridges). The latter two are located near the central district of Okayama city. Rain-water samples were collected as three successive fractions at our campus and bottled into polyethylene vessels through a polyethylene-made filter funnel (diameter: 21 cm). After being filtered through a membrane filter (pore size: 0.22 µm, Millipore), the samples were chromatographed as soon as possible. If necessary, the samples were stored in a refrigerator.

As an illustration, chromatograms of the water samples (river, rain and snow) are shown in Fig. 7. The peak resolution between NH₄⁺ and K⁺ was quite satisfactory. The cation concentrations obtained are shown in Table 1. These values agree fairly well with those obtained by the AAS and NH₄⁺-selective electrode methods.

<table>
<thead>
<tr>
<th>Table 1 Cation concentrations in river and rain water</th>
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<tbody>
<tr>
<td>Water</td>
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<tr>
<td>-----------------------------------------------</td>
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<tr>
<td>Tap water</td>
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<tr>
<td>Asahi 1&lt;sup&gt;16&lt;/sup&gt;</td>
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<td>Asahi 2&lt;sup&gt;16&lt;/sup&gt;</td>
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<td>Asahi 3&lt;sup&gt;16&lt;/sup&gt;</td>
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<td>Zasu</td>
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<td>Takahashi</td>
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<td>Yoshii</td>
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<tr>
<td>Rain water 1&lt;sup&gt;16&lt;/sup&gt;</td>
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<tr>
<td>Rain water 2&lt;sup&gt;16&lt;/sup&gt;</td>
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<tr>
<td>Rain water 3&lt;sup&gt;16&lt;/sup&gt;</td>
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<sup>a</sup> Proposed method. <sup>b</sup> Ion-selective electrode method. <sup>c</sup> Katsuragi bridge (Br.) d. Nakahara Br. e. Shin-Tsurumi Br. f. Tsukimi Br. g. Collected at Dec. 9, 1988; 12:40 – 17:40. h. 17:40 – 19:40. i. 19:40 – next morning.
The ionic compositions of the three river-water samples were found to be almost the same. From Table 1 it is obvious that the concentration of Ca\(^{2+}\) in the Takahashi river is markedly high. This result can well be explained by taking into account the fact that only the Takahashi river flows through a limestone area at its upper stream. The water sample taken at Tsukimi bridge contained more cations than the other samples collected up-stream; this presumably indicates the presence of water pollution due to human activities.

It was found that, except for NH\(_4^+\), the rain water contains considerably smaller quantities of cations than does the river water. The cation contents in the rain water gradually decreases with an increase in the duration of rainfall, as expected.

References


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