Separation of Dissolved Aluminum in Neutral/Slightly Basic River Water by Cation-Exchange Chromatography with Fluorometric Detection of the Lumogallion–Aluminum Complex

Hirokazu Hara,* **Miyuki Fujiwara, and Hiroko Kamiyama**

Department of Chemistry, Faculty of Education, Shiga University, Otsu, Shiga 520-0862

Received July 7, 2003; E-mail: hara@sue.shiga-u.ac.jp

The separation of dissolved aluminum in neutral/slightly basic river (Seta River) water was carried out using high-performance cation-exchange chromatography with a gradient elution of calcium ion in a dilute nitric acid solution (pH 4) and fluorometric detection of the lumogallion–aluminum complex. Although three peaks may appear, which correspond to species having a charge of less than +1, +2 and +3, only one major peak at the "3+" position appeared. From the sample pH and this result of separation, the main species of dissolved aluminum was concluded to be $Al(OH)_4^-$. In order to evaluate whether the elution was complete or not, the peak areas obtained with and without the cation-exchange column were compared. For an accurate evaluation of the elution peak, the residual solution of the solvent extraction with the 8-quinolinol/chloroform system was used. The elution of dissolved aluminum from the cation-exchange column was found to be incomplete (or not quantitative); i.e., the percentage of eluted aluminum was 79 and 70% for two Seta River water samples in October and January, respectively. The chemical form of the aluminum species which was adsorbed in the cation-exchange column is discussed.

Aluminum is the third most abundant element in the earth crust. It has been believed to be a non-toxic element for a long time. However, its increased concentration in lakes and rivers due to acidification of the environment has recently occurred in North America and Europe, and has caused serious damage to some aquatic life.[1,2] Moreover, aluminum has been proven to be toxic to the human nervous system if it accumulates in the human brain through an unfortunate incident of dialysis dementia.[3] Reports have been published, in which a positive correlation between the aluminum concentration in drinking water and Alzheimer's disease is observed through epidemiological research.[4,5] Its toxicity was influenced by co-existing ligands, such as fluoride or silicate.[6,7] This fact suggests that the speciation of aluminum in drinking water is very important.

Lake Biwa, the largest lake in Japan, is located in Shiga prefecture. The lake water flows out from the Seta River. The pH of Seta River water is always above 7.0 and may be increased up to 9 due to the high activity of phytoplankton in the summer season. The water is actually used as drinking water not only for people living in Shiga, but also for over 13 million people living in the Kinki district. Lake Biwa is sometimes compared to a water jar for the Kinki district.

The chemical behavior of aluminum in Lake Biwa has been examined from a limnological standpoint.[8–11] The dissolved aluminum concentration in the surface water of both the northern and southern parts of the lake shows a seasonal variation: high during the summer and autumn and low in the winter.[8,10] The cause of this phenomenon was examined by Kanao-Koshikawa et al., who concluded that the pH of the lake, measured one month before, is the main factor.[10] We also found such a seasonal variation of dissolved aluminum concentration in the Seta River,[12,13] which correlated well to the pH measured immediately after sampling. The concentration range of dissolved aluminum in the Seta River is between 0.5 and 5×10^{-7} mol dm^{-3}.

Ion-exchange chromatography has been widely used for the speciation of aluminum in drinking water,[14,15] lake water,[16,17] soil extracts,[18,19] and so on. The aluminum species are separated according to their charge; i.e., Al^{3+}, "2+" charged species, such as AlF^{2+}, and "1+"; neutral or negatively charged species, such as AlF_2^+, AlF_3 and Al–organic complexes, respectively.

Recently, cation-exchange HPLC with postcolumn fluorometric detection of an aluminum lumogallion complex has been developed and applied to the analysis of acidified lakewater.[16] This method uses the gradient elution of divalent calcium ion for effective separation, and is very sensitive to detect even 1×10^{-9} mol dm^{-3} aluminum. We successfully applied this method to the speciation of dissolved aluminum in acidic rain water into three categories, i.e., free Al^{3+}, aluminum fluorides and other forms.[20]

Although there have been many studies of speciation of aluminum in acidic water samples by cation-exchange chromatography, its application to neutral water samples has been relatively few.[14,15] In present work, we tried to apply this method to the analysis of Seta River water as a typical example of neutral/slightly basic water samples. We first optimized the analytical system in order to obtain a correct chromatogram. We then considered the chemical species of dissolved aluminum based on the chromatogram from which the baseline chromatogram was subtracted. To obtain a correct baseline, a residual solution of solvent extraction was used. We also compared the peak area with and without a cation-exchange column in order to examine whether the chromatographic elution was quantitative or not.

Published on the web January 13, 2004; DOI 10.1246/bcsj.77.133

Experimental

Reagents. Once-distilled water was further purified using a Millipore Milli-Q Labo system. Guaranteed reagent-grade chemicals were obtained from Nakalai tesque (Kyoto, Japan), unless otherwise noted. Ultrahigh-purity nitric acid, Tamapure AA-100 was supplied from Tama Chemicals Co., Ltd. (Kanagawa, Japan). Calcium nitrate tetrahydrate (Cat. no. C4955, SigmaUltra) was purchased from Sigma (St. Louis, MO, USA). The postcolumn reagent solution was 0.05 $\mathrm{mmol\,dm^{-3}}$ lumogallion (DOJINDO, Kumamoto, Japan) dissolved in 0.2 $\mathrm{mol\,dm^{-3}}$ acetate buffer (pH 5.2). Two eluents for gradient elution were used: pH 4.0 HNO_3 and 0.0165 $\mathrm{mol\,dm^{-3}}$ $Ca(NO_3)_2$ (the pH was also adjusted to 4.0 by HNO_3). Aluminum standards were prepared in plastic volumetric flasks. A stock standard (10^{-2} $\mathrm{mol\,dm^{-3}}$) was prepared by dissolving 0.4744 g of $AlK(SO_4)_2 \cdot 12H_2O$ into 100 mL of 10^{-3} $\mathrm{mol\,dm^{-3}}$ nitric acid. The pHs of the 0–10 × 10^{-7} $\mathrm{mol\,dm^{-3}}$ aluminum standard solutions were adjusted to ca. 4.0 by adding 0.1 mL of 0.1 $\mathrm{mol\,dm^{-3}}$ nitric acid into 100 mL plastic volumetric flasks.

Apparatus. Figure 1 shows a schematic diagram of the HPLC system. The basic scheme was the same as that of Sutheimer and Cabaniss.[16] Two Shimadzu LC-10AD chromatographic pumps were used to create a concentration gradient of divalent calcium ions. All of the sapphire plungers of each pump were replaced by a zirconia ceramic plunger in order to decrease the possibility of aluminum elution from the pump. The sum of the flow rates was kept at 0.9 $\mathrm{mL\,min^{-1}}$. A single plunger pump (Nihonseimitsu Model SP-T-2501-U, Tokyo, Japan) was used to deliver the reagent solution. The pulse was effectively damped using a damper (GL Science Model HPD-2, Tokyo, Japan). The flow rate was set at 0.4 $\mathrm{mL\,min^{-1}}$.

In order to remove residual aluminum ions from the eluents, a precolumn was placed just after each main pump. The precolumn was prepared by placing a TSK-8HQ chelating resin in a PEEK column (4.7 mm i.d., 15 cm long). The TSK-8HQ chelating resin was based on a TSK-Gel TOYOPEARL HW-65F (Cat. no. 07465, Tosoh, Tokyo, Japan), on which 8-quinolinol was covalently fixed, prepared according to a method reported by Landing et al.[21] It has long-term stability and shows excellent efficiency for removing aluminum ions.

We also used a second precolumn after the TSK-8HQ column in order to remove residual fluoride. The precolumn was filled with a cation-exchange resin (Dowex 50W-X8 200–400 mesh) treated with a solution of zirconium(IV) bis(nitrate) oxide ($Zr(NO_3)_2O$), prepared according to a method reported by Kokubu et al.[22]

The rotary injection valve was made of stainless steel (Rheodyne Model 7010, CA, USA) fitted with a PEEK 500 µL injection loop. To separate aluminum species according to their charge, a cation-exchange column (Mitsubishi Kagaku MCI-Gel, SCK01, 6 mm i.d., 50 mm long, Tokyo, Japan) was used. This column was made of a copolymer based on polystyrene and divinylbenzene having a sulfonate functional group, and was usually used for the ion-chromatographic separation of singly-charged cations. In order to avoid the accumulation of adsorbed species, the column was washed with 0.1 $\mathrm{mol\,dm^{-3}}$ nitric acid after a series of the separation experiments were finished. Then, nitric acid was replaced by ultrapure water until the pH became 4 or above.

Two PEEK mixing coils (0.5 mm i.d., 5 m long) were used, the first maintained at 60 °C in a water bath, while the second remained at room temperature. PEEK tubing was used in the whole system with some exceptions [otherwise, a poly(tetrafluoroethylene) (= PTFE) tube was used]. Fluorescence was detected by a JASCO (Nihonbunkou, Tokyo, Japan) FP2025 detector equipped with a 150 W xenon lamp, a 16 µL quartz flow cell, and a photomultiplier tube. The excitation and emission wavelengths were 500 and 595 nm, respectively. The detector signals were transmitted every 0.5 s and recorded by a microcomputer using JASCO BOWIN software running on a Windows NT operating system.

The fluoride concentration in the eluents before and after passing through the Zr-column was measured potentiometrically using an Orion fluoride ion-selective electrode (Model 96-09BN). Detection limit was 1 × 10^{-8} $\mathrm{mol\,dm^{-3}}$ using an acidic buffer[23] composed of 2-aminopropionic acid and HCl.

Determination of Total Dissolved Aluminum. The total dissolved aluminum was determined by the same HPLC system without Zr and SCK01 columns. Samples were injected through a 0.22 µm disk filter (Millipore Millex-GS, MA, USA), and the peak area during 10 min after the sample injection was recorded. A calibration graph was prepared using 0, 2, 4, 6, 8, and 10 × 10^{-7}

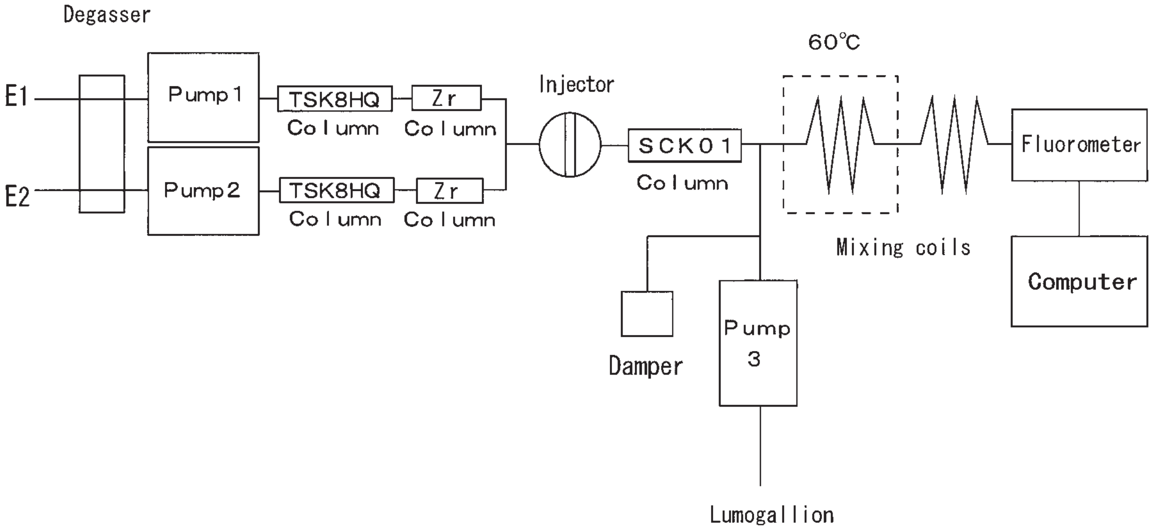

Fig. 1. Schematic diagram of the chromatographic system. E1: pH 4.0 nitric acid. E2: 0.0165 $\mathrm{mol\,dm^{-3}}$ calcium nitrate (pH was adjusted to 4.0 by nitric acid). The concentration of lumogallion was 0.05 $\mathrm{mmol\,dm^{-3}}$.

mol dm^{-3} aluminum standard solutions. The correlation coefficient of the calibration graph usually exceeded 0.999. The blank aluminum level calculated from the intercept of a calibration graph was usually below 3×10^{-8} mol dm^{-3}. To calculate the concentration of a sample, this blank level was ignored. The mean value of duplicate or triplicate analysis was used to calculate the sample concentration. The relative standard deviation of the three peak areas was usually below 1.0% for a sample containing above 1×10^{-7} mol dm^{-3} total dissolved aluminum, and became larger for more dilute samples.

Separation of Aluminum Species Based on Charge. The flow rate of the two eluents, pH 4.0 HNO_3 and 0.0165 mol dm^{-3} $Ca(NO_3)_2$ (pH 4.0), was adjusted to 0.082 and 0.818 mL min^{-1}. After mixing, the concentration of calcium ions was 0.015 mol dm^{-3}. One minute before the sample injection, the flow rates of both pumps were exchanged. Then, 1.5 min after sample injection, gradient elution began. During 30 min, the flow rates were linearly changed to preset values with time. Namely, the flow rate of the pH 4.0 HNO_3 changed from 0.082 mL min^{-1} to 0.818 mL min^{-1} instantaneously, remained for 2.5 min, then returned back to 0.082 mL min^{-1} after 30 min, and vice versa. The total recording time was usually set to 90 min.

The procedure produced three distinctive peaks if positively charged species of +1 or less, +2, and +3 were contained in a sample solution. The peak area of each peak was obtained from a chromatogram of the sample after subtracting the chromatogram of the corresponding baseline, which was measured just before the sample. In order to improve the fitness of both chromatograms, the drift of the background level of fluorescence was corrected by tilting each chromatogram so as to take both ends to be zero. We call this "a leveling treatment", and show two chromatograms after this treatment in one figure.

The Baseline Solution. The residual solution from solvent extraction was used for a baseline. The extraction of aluminum ions using 100 mL of a river water sample solution after filtration was repeated three times with 20 mL of 0.1% 8-quinolinol/chloroform in a PTFE separatory funnel. The residual solution was washed once with 20 mL of chloroform to remove 8-quinolinol in the aqueous phase. The extraction procedure was performed without any buffer. The pH of the baseline solution was almost unchanged, or slightly higher than that before extraction. The concentration of 8-quinolinol was high enough to ensure that the concentration of dissolved aluminum decreased to 2–9% of that before extraction; i.e., on the order of 10^{-9} mol dm^{-3}.

Synthetic Seta River water was prepared, which had nearly the same ion concentrations (except nitrate ion) and pH as the Seta River for the purpose of a comparison. The major ion concentrations of Seta River water during one year were given in a previous paper.[12] The pH of the synthetic Seta River water was adjusted to 7.2–7.5 by adding sodium hydrogencarbonate ($NaHCO_3$) and calcium carbonate ($CaCO_3$).

River-Water Sampling. One or two liters of Seta River water was sampled at a spot near to the bus stop of Shiga-Dai Mae, which is located on the west side of the river. The water characteristics at the sampling spot are nearly the same as those of Nanko (the southern part of Lake Biwa) water. The pH of a sample was measured on site with a visual color pH indicator. Upon returning to the laboratory, the sample pH was again measured with a pH glass electrode. Each sample was filtered using a plastic funnel equipped with a 0.45 μm cellulose acetate membrane filter (Type HAWP, Millipore) in order to remove any suspended particulate matter. The filtrate was injected into the FIA system through a disk filter (Millipore Millex-GS 0.22 μm). The filtered water samples were stored in a thermostated bath at 30 °C.[13] (The storage temperature was at first determined in order to investigate the effect of temperature on the total dissolved aluminum concentration during the storage of winter samples. Against our expectation, the concentration was relatively stable during one month storage after sampling, which means that the temperature increase had no relation to the concentration increase in the summer season.[13] The storage below freezing temperature gave rise to a very poor recovery of dissolved aluminum from the thawing sample. We had no experience of sample storage in a refrigerator, while Andrén reported the effects of storage on stream water fractionated for labile and non-labile aluminum[24] at 4 ± 2 °C. The stability of monomeric aluminum during storage for one or two months depended on the water characteristics of the sample.[24])

Results and Discussion

Importance of the Baseline Solution. In this system, the baseline level depends on the residual aluminum concentration in the eluents (e.g., usually higher in the calcium nitrate eluent), and also changes according to the mixing ratio of the eluents during the gradient elution process. Moreover, a small peak at the retention time of Al^{3+} inevitably appeared because of the gradient elution, even if ultrapure water was injected as a sample. The residual aluminum ion in the eluents is concentrated in the cation-exchange column at the first stage of gradient elution when the calcium concentration decreases to 0.0015 mol dm^{-3}; then it will be eluted as the calcium concentration increased. Thus, a correct baseline is indispensable for evaluating the peak area quantitatively.

In a previous study,[20] we used ultrapure water for a baseline solution. However, we found that the shape of the thus-obtained baseline from ultrapure water did not fit the chromatogram of Seta River water well, probably because of the ionic strength difference. We then used a synthetic solution having nearly the same ion concentrations as those of the Seta Rive water as a baseline solution, but it was not satisfactory. Finally, the residual solution of the solvent extraction was tested to give a satisfactory result.

Necessity of the Zr-Column. Even if no aluminum fluorides exist in a sample solution, they can give a small peak at the "2+" position, because of the reaction between the aluminum ion in a sample solution and fluoride in the eluents. Figure 2 shows the effect of the Zr-column to remove fluoride. Apparently, the "2+" peak height decreased when the Zr-column was inserted in both lines (see Fig. 1). If fluoride could be completely removed, it would be reasonable to expect that the "2+" peak would disappear. Interestingly, nearly the same peaks as those shown in the figure were obtained when the Zr-column, inserted in the calcium nitrate eluent, was removed. This result suggests that the fluoride in the pH 4 nitric acid eluent mainly caused the small peak at the "2+" position. However, the concentration of fluoride in the pH 4 nitric acid eluent, itself, was too low to be measured by the fluoride ion-selective electrode method (below 1×10^{-8} mol dm^{-3}). It increased to be about 1×10^{-7} mol dm^{-3} when sampled at just before the entrance of the cation-exchange column. Thus, we concluded that fluoride in the pH 4 nitric acid eluent came from some parts of the chromatographic system; e.g., it might have been eluted from the chromatographic pump. We did not further examine

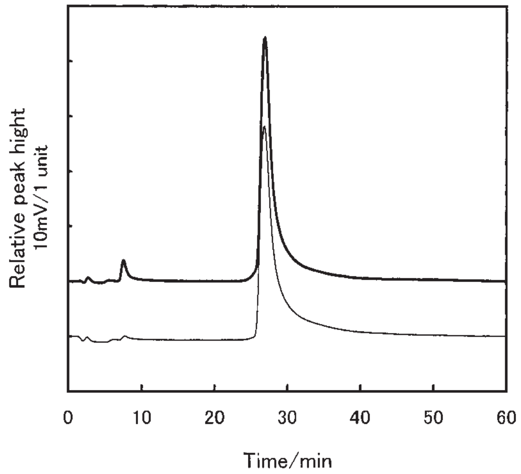

Fig. 2. Effect of Zr-column on the chromatogram of Seta River water sampled on October, 8, 2002. Upper curve: without Zr-column, lower curve: with Zr-column at each eluent line.

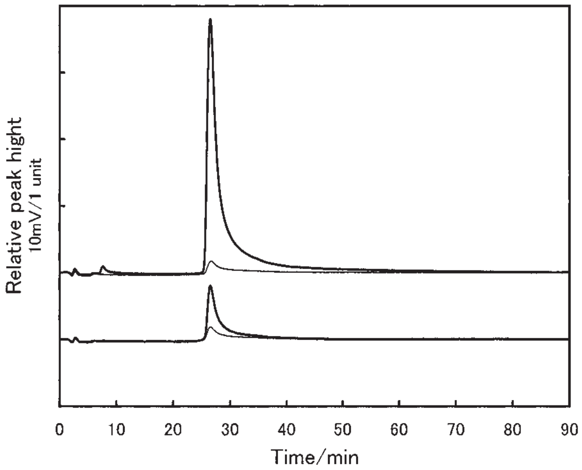

Fig. 3. Chromatogram of Seta River water sampled on October, 8, 2002 (upper curve) and January, 28, 2003 (lower curve). Baseline chromatogram was taken with the residue of the solvent extraction by 8-quinolinol/chloroform prepared from each sample.

the origin of fluoride, because the "2+" peak disappeared in winter samples containing very low concentrations of aluminum ion.

Result of Separation. Figure 3 shows chromatograms of Seta River water in two seasons when the dissolved aluminum concentration was relatively high and low, together with the corresponding baselines. Irrespective of the season, one major peak appeared at the "3+" position (Similar results were obtained in spring and summer samples.) In this system, Al^{3+} and its hydrolysis species, such as $Al(OH)_2{}^{+}$, $Al(OH)_3$ and $Al(OH)_4{}^{-}$, all give only one peak at the "3+" position.[16] It is well known that $Al(OH)_4{}^{-}$ is dominant at pHs greater than 7,[25,26] Al^{3+} may be formed from $Al(OH)_4{}^{-}$ by reactions with acidic eluents. This result confirmed the report of Koshikawa,[11] in which the major part of the dissolved aluminum in Lake Biwa was suggested to be aluminum hydroxides and/or very weakly bound organic complexes. It also corresponds well to the equilibrium model calculation performed by Bi et al.[26] for surface water of low ionic strength. Most of the truly dissolved aluminum is concluded to be in the form of $Al(OH)_4{}^{-}$ in Seta River water with a weak alkaline pH.

The very small peak appearing at the "2+" position in Fig. 3 is concluded to be a false peak, which was produced by the reaction of aluminum ion in the sample and fluoride in the pH 4 nitric acid eluent, as mentioned above. According to the equilibrium calculation of Bi et al.,[26] aluminum fluoride should not be formed at a pH region above 7.0.

We concluded that the peak appearing at the "1+" position was also a false peak, which was caused by the shock of sample injection. This small peak always appeared in the chromatogram of a sample and its corresponding baseline in a similar manner. Thus, this peak will almost disappear after subtracting the baseline. Mitrović et al. separated dissolved aluminum in surface water (pH 7.6) by cation-exchange fast protein liquid chromatography.[27] Aluminum species gave only one peak at the solvent front, the result of which was interpreted as the elution of $Al(OH)_4{}^{-}$ and aluminum humate. The complex of aluminum and humic substances has a negative charge in pH 6.0 (or above).[27] Although the aluminum hydroxide species can be separated in their system, it is impossible to separate $Al(OH)_4{}^{-}$ and aluminum humate, because they are both negatively charged species in neutral/slightly basic water. In the present system, the separation of these species is possible because $Al(OH)_4{}^{-}$ is decomposed into Al^{3+} by acidic eluents, while aluminum humate elutes at the solvent front.[28] Thus, we concluded that there are no negatively-charged aluminum organic complexes in Seta River water, at least in both samples, shown in Fig. 3.

Quantitative Elution. It has been well recognized that there are several species of aluminum in natural waters, which are adsorbed by a cation-exchange column. Driscoll utilized this fact to construct the original fractionation scheme.[29] Labile monomeric aluminum, such as aluminum sulfate, fluoride, and hydroxide complexes, was separated from non-labile monomeric aluminum, such as monomeric alumino–organic complexes, by passing an aliquot of each sample through a cation-exchange column.[29] Only non-labile monomeric aluminum was thought to be eluted.

Using the present method, no result has been reported on the quantitative elution of neutral natural water samples. For a quantitative evaluation as to whether the elution of aluminum species from the cation-exchange column was complete or not, we compared the peak area recorded with and without the cation-exchange column. We assumed that the peak area without the cation-exchange column represented the total aluminum concentration, which can be reacted with lumogallion. Not only labile monomeric aluminum, but also aluminum organic complexes with humic acid, were reported to be measured; however, lumogallion did not react with polymeric aluminum.[30] In order to obtain the sum of the peak area appearing on the cation-exchange chromatogram, we constructed a chromatogram of Seta River water in which the baseline was subtracted. By this treatment, not only the aluminum concentrated on the column at the first stage of the gradient elution, but also the aluminum contained in the residual solution (which re-

Table 1. Comparison of the Peak Area before and after Separation with the Cation-Exchange Column

Date of sampling	[T-Al]	Peak area/V s					Ratio
	μmol dm^{-3}	Total a)	"2+"	"3+"	Base a)	Sum b)	Sum/Total
Oct. 8, 2002	0.385	8.60	0.12	6.55	0.16	6.83	0.79
Jan. 28, 2003	0.0752	1.63	0	0.99	0.15	1.14	0.70

a) Peak area of the sample and the baseline solutions measured without the cation-exchange column. b) Sum of the peak area corresponding to the "2+" and "3+" peaks plus Base.

mained after the extraction process) was subtracted. The latter peak area of the baseline solution was measured without the cation-exchange column previously and added afterwards for calculating the peak-area ratio.

Table 1 gives the results of a peak-area analysis of the chromatograms shown in Fig. 3. The results mean that the only 79 or 70% of the aluminum in the sample solution eluted from the column. Although we have no explicit data on the reproducibility of the separated "3+" peak area, we have other data for the Jan. 28 sample taken with a different experimental condition. Namely, the "3+" peak area was 0.988 V s (99.4% of 0.994 V s) when the time for the gradient elution was reduced from 30 min to 4.5 min, and also the peak area for T-Al was measured on the same day to be 1.60 V s (98.2% of 1.63 V s), and finally the peak area ratio was 71%. We estimated that the reproducibility of the peak area ratio should be within ±5%. We concluded that the difference of the peak areas with and without the cation-exchange column was statistically significant.

Thus, 20–30% of the dissolved aluminum was adsorbed by the cation-exchange column, although it reacted with lumogallion. First, we discuss the chemical form of the adsorbed species. According to Bloom and Erich,[31] the soluble aluminum in natural water has at least 6 different forms. That is, 1) the fine colloidal mineral aluminum, 2) aluminum associated with organic macromolecules such as fulvic and/or humic acids, 3) aluminum adsorbed on the surface of colloidal mineral aluminum, 4) low-molecular weight organic complexes, 5) monomeric inorganic complexes, and 6) hydroxy-polymers. As for the form of 1), it is well known that colloidal aluminosilicates are contained in river and/or lake water.[32] However, colloidal clay particles, such as aluminosilicates, do not react with lumogallion. As for the form of 6), polymeric aluminum hydroxides also could not react with lumogallion,[30] although they were easily adsorbed by a cation-exchange fast protein liquid chromatography (FPLC) column.[27] (Even $Al(OH)_4^-$ was adsorbed by a cation-exchange FPLC column as reported by Mitrović et al.[33]) Among them, the forms of 2), 4), and 5) can be measured by the lumogallion method.[30] From the result of separation, the forms of 2) and 4) do not exist in Seta River water and the form of 5) should be aluminum hydroxides only; they have to elute completely as Al^{3+}. Accordingly, the only possible adsorbed species is the form of 3). This form of aluminum is said to play an important role in the seasonal concentration change of dissolved aluminum in Lake Biwa.[10] If this form of aluminum could be measured by the lumogallion method, the aluminum of this form may be regarded as the adsorbed species.

However, there is no colloidal mineral aluminum in a synthetic aluminum solution. In our preliminary experiment, the peak area ratio of the Al standard solution (4×10^{-7} mol dm^{-3}, pH 4) with and without a cation-exchange column decreased from 0.99 to 0.72 after neutralizing it to pH 7.2 with a sodium carbonate solution (The baseline solution was pH 4 nitric acid and its pH became 7.85 by adding the same amount of sodium carbonate solution.). This result means that the adsorbed chemical species are formed by neutralization without colloidal mineral aluminum. Thus, we come to the conclusion that the adsorbed chemical species is a colloidal aluminum trihydroxide ($Al(OH)_3$).

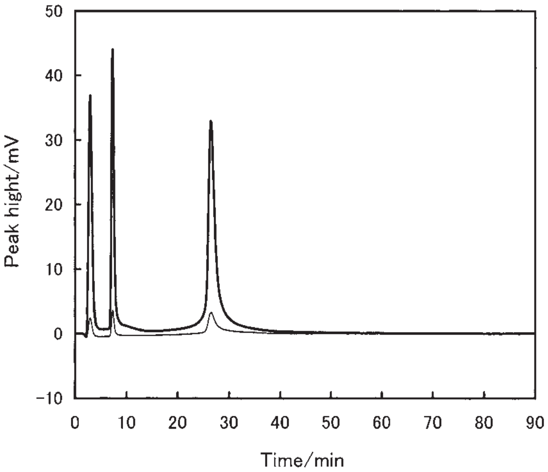

Fig. 4. Chromatogram of acidified Seta River water sampled on October, 8, 2002. The pH of the sample and the baseline solution were adjusted to 3.61 and 3.66, respectively, by adding 0.01 mol dm^{-3} nitric acid.

Even if this is true, the species might be hardly decomposed at pH 4 or less. We also tried to separate the aluminum species in Seta River water immediately after acidifying it to pH 3.6 with nitric acid. Figure 4 shows the chromatogram, in which distinct peaks at the positions of "1+" and "2+" can be observed. These peaks indicate the formation of aluminum fluorides (the concentration of fluoride in Seta River water is ca. 6.2×10^{-6} mol dm^{-3}). The peak area ratio with and without the cation-exchange column was 0.98. This result suggests that the adsorbed aluminum species (even if it were colloidal) at neutral pH may be easily dissolved at pH 3.6 (but not at pH 4.0). At present, we have no more data to support the above deduction. Further research is necessary to determine the chemical form of the adsorbed species explicitly.

In order to apply cation-exchange chromatography to the speciation study of aluminum, we think that it necessary to assure quantitative elution. It is not desirable that a portion of the injected species is adsorbed on a column (unfortunately as was the case in this study), because the reliability of the result of speciation analysis decreases. Namely, the percentage of the adsorbed species may be easily changed if some of the experimental conditions are varied. Thus, we have to try first to find an analytical condition which enables quantitative elution on this column. If this will be difficult, we will try to use another kind of column, or try to separate the colloidal species beforehand by using a new membrane technique.[34]

Conclusion

We have applied cation-exchange chromatography to the separation of aluminum species in neutral/slightly basic river water (the water characteristic is similar to that of the southern part of Lake Biwa). We first tried to obtain a correct chromatogram by improving several points concerning the analytical conditions. One such improvement was to use a residual solution of solvent extraction as a baseline. The chromatograms of two samples taken in different seasons, when the dissolved aluminum concentration was relatively high and low, showed only one major peak at the position of "3+" charged species, i.e., Al^{3+}. This species may be formed by the reaction with acidic eluents from $Al(OH)_4^-$. The chemical form of dissolved aluminum in Seta River water was concluded to be mainly $Al(OH)_4^-$. We also compared the peak area with and without a cation-exchange column. The sum of the peak areas with a column was smaller than that measured without a column by about 20–30%. This portion of aluminum species was adsorbed on a cation-exchange column, although the both eluents were acidic (pH 4). We discussed the chemical form of the adsorbed species, and deduced that a fine colloidal $Al(OH)_3$ was adsorbed. We will pursue the analytical condition of quantitative elution in a future study.

We thank E. Yoneda and H. Yamamoto for their assistance with some of the experiments.

References

1 W. H. Hendershot, F. Courchesne, and D. S. Jeffries, "The Environmental Chemistry of Aluminum," 2nd ed, ed by G. Sposito, CRC Press, Boca Raton, FL (1996), Chapter 10, pp. 419–449.

2 "Sanseiu Kenkyu to Kankyo Siryou Bunseki (Research on Acid Rain and Environmental Sample Analysis)," ed by K. Satake, Aichi Shuppan, Tokyo (2000).

3 V. V. Rozas, F. K. Port, and R. E. Easterling, *J. Dial.*, **2**, 459 (1978).

4 D. R. C. McLachlan, C. Bergeron, J. E. Smith, D. Boomer, and S. L. Rifat, *Neurology*, **46**, 401 (1996).

5 E. Gauthier, I. Fortier, F. Courchesne, P. Pepin, J. Mortimer, and D. Gauvreau, *Environ. Res.*, **84**, 234 (2000).

6 W. F. Forbes and N. Agwani, *J. Theor. Biol.*, **171**, 207 (1994).

7 V. Rondeau, D. Commenges, H. Jacqmin-Gadda, and J.-F. Dartigues, *Am. J. Epidemiol.*, **152**, 59 (2000).

8 T. Hori, Y. Sugiyama, M. Kanao, M. Nagai, N. Taniguchi, M. Sugiyama, and T. Fujinaga, *Jpn. J. Limnol.*, **57**, 183 (1996).

9 M. Nagai, M. Sugiyama, and T. Hori, *Limnology*, **2**, 147 (2001).

10 M. Kanao-Koshikawa, M. Sugiyama, and T. Hori, *Limnology*, **3**, 1 (2002).

11 M. Koshikawa, *Kokuritsu Kankyo Kenkyusho Nenpo*, **2002**, 235.

12 H. Hara, Y. Kobayashi, and A. Ueno, *Shiga Daigaku Kyouikugakubu Kiyo, III: Shizen Kagaku*, **51**, 15 (2001).

13 H. Hara, M. Fujiwara, H. Kamiyama, and E. Yoneda, *Shiga Daigaku Kyouikugakubu Kiyo, III: Shizen Kagaku*, **52**, 1 (2002).

14 P. Jones, *Int. J. Environ. Anal. Chem.*, **44**, 1 (1991).

15 P. Jones and B. Paull, *Anal. Proc.*, **29**, 402 (1992).

16 S. H. Sutheimer and S. E. Cabaniss, *Anal. Chem.*, **67**, 2342 (1995).

17 K. Tsunoda, T. Umemura, K. Ohshima, S. Aizawa, E. Yoshimura, and K. Satake, *Water, Air, Soil Pollut.*, **130**, 1589 (2001).

18 K. Tsunoda, T. Yagasaki, S. Aizawa, H. Akaiwa, and K. Satake, *Anal. Sci.*, **13**, 757 (1997).

19 E. Yamada, T. Hiwada, T. Inaba, M. Tokukura, and Y. Fuse, *Anal. Sci.*, **18**, 785 (2002).

20 H. Hara, H. Kobayashi, M. Maeda, A. Ueno, and Y. Kobayashi, *Anal. Chem.*, **73**, 5590 (2001).

21 W. M. Landing, C. Haraldsson, and N. Paxéus, *Anal. Chem.*, **58**, 3031 (1986).

22 N. Kokubu, T. Kobayashi, and A. Yamasaki, *Bunseki Kagaku*, **29**, 106 (1980).

23 H. Hara, K. Yabuuchi, M. Higashida, and M. Ogawa, *Anal. Chim. Acta*, **364**, 117 (1998).

24 C. Andrén, *Water, Air, Soil Pollut.*, **85**, 811 (1995).

25 S. Bi, *Analyst*, **120**, 2033 (1995).

26 S. Bi, S. Du, and D. L. Correll, *Int. J. Environ. Anal. Chem.*, **68**, 479 (1997).

27 B. Mitrović, R. Milačič, B. Pihlar, and P. Simončič, *Analusis*, **26**, 381 (1998).

28 S. H. Sutheimer and S. E. Cabaniss, *Geochim. Cosmochim. Acta*, **61**, 1 (1997).

29 C. T. Driscoll, *Int. J. Environ. Anal. Chem.*, **16**, 267 (1984).

30 S. H. Sutheimer and S. E. Cabaniss, *Anal. Chim. Acta*, **302**, 112 (1995).

31 P. R. Bloom and M. S. Erich, "The Environmental Chemistry of Aluminum," 2nd ed, ed by G. Sposito, CRC Press, Boca Raton, FL (1996), Chapter 1, pp. 1–38.

32 K. Inoue and M. Yoshida, *Soil Sci. Plant Nutr.*, **36**, 461 (1990).

33 B. Mitrović, R. Milačič, and B. Pihlar, *Analyst*, **121**, 627 (1996).

34 L. Weng, E. J. M. Temminghoff, and W. H. Van Riemsdijk, *Water Res.*, **36**, 4215 (2002).