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Determination of Aluminium in Natural Waters by Ion-Pair Reversed-Phase Partition HPLC

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Synopsis. An ion-pair reversed-phase partition high-performance liquid chromatography-spectrophotometric detection system with 2,2′-dihydroxyazobenzene has been successfully applied to the determination of μg dm^{-3} level of aluminium in natural waters. The detection limit is 0.2 μg dm^{-3} in pure solution, and 1 μg dm^{-3} for total aluminium in water sample. The relationship between the aluminium concentration and pH value of the ground waters is also discussed.

Aluminium ion in natural waters has been the focus of increasing attention concerning with the effects of acid precipitation on terrestrial and aquatic ecosystems.[1-3] This element is also of geochemical interest because of its important role in the interaction between water and silicate minerals.[4,5] However, the values reported for trace aluminium in natural waters are still relatively rare, mainly due to the analytical difficulties. Graphite furnace atomic absorption spectrophotometry, the most commonly used technique for trace aluminium, is often limited due to the interferences from the foreign substances.

In our previous studies, it has been demonstrated that an ion-pair (IP) reversed-phase (RP) partition high performance liquid chromatography (HPLC)-spectrophotometric method offers a simple, highly sensitive, and selective method for trace metals, based on its complexation with 2,2′-dihydroxyazobenzene (DHAB).[6,7] The anionic chelates of V^{V}, Co^{II}, Al^{III}, and Fe^{III} ions are separated on C_{18}-bonded silica packing with IP mode and are detected at 510 nm. While, equal amounts of a number of other metal ions such as Ca^{II}, Cd^{II}, Cr^{II}, Cu^{II}, Hg^{II}, Mg^{II}, Mn^{II}, Mo^{VI}, Ni^{II}, Pb^{II}, and Zn^{II} give no elution peaks due to the labile nature of their DHAB chelates.[7] The detection limit for aluminium (0.2 μg dm^{-3}) is comparable to that of a HPLC-spectrophotometric detection system with salicylaldehyde benzoylhydrazone[8] and better than those with the other azo dyes[7] and that with 8-quinolinol by the use of a mobile phase containing the chelating reagent.[9] This system was applied to the determination of trace aluminium in the human sera of dialysis patients.[10]

The object of this work is to develop a sensitive and rapid method applicable to ppb levels of aluminium in natural waters based on IPRP-HPLC with DHAB. The method is essentially free from interferences of other ions normally found in natural waters. Therefore, no preparatory procedures for separation or concentration are required. It is applicable to the direct analysis of a small volume of water samples. A consistent feature of the data presented here is the correlation between aluminium concentration and pH value of the ground water.

Experimental

Apparatus and Reagents. The HPLC setup consisted of a Shimadzu LC-5A pump unit, a SPD-2A spectrophotometric detector and a Rheodyne 7125 loop injector (0.1 cm^3). The detector setting of 0.01 absorbance unit full-scale (AUFS) at 510 nm was used for 1 mV recorder output. A LiChroCART RP-18 column (4 mm i.d. ×120 mm length from Merck) was used. The reagent, DHAB, was used as received from Dojindo Laboratories and the solution (ca. 1.0×10^{-3} mol dm^{-3}) was prepared by dissolving it in an slightly alkaline (pH 9—10) aqueous solution containing 4 wt% PONPE-20 (α-(4-(nonylphenyl)-ω-hydroxypoly(oxyethylene) with 20 oxyethylene units from Tokyo Kasei Kogyo Co., Ltd.). Potassium hydroxide and hydrochloric acid were of ultrapure grade (Kanto Chemical Co., Inc.). As a mobile phase, an aqueous methanol (61.7 wt%, pH 8.0) containing 6×10^{-3} mol kg^{-1} tetrabutylammonium bromide (TBABr), 2×10^{-3} mol kg^{-1} trihydroxy(methylamino)methane (THMAM) and 10^{-4} mol kg^{-1} disodium ethylenediaminetetraacetate (EDTA) was used. The standard solution of aluminium was prepared by dissolving aluminium chloride in 0.1 mol dm^{-3} nitric acid solution and was standardized by complexometric titration with EDTA. All other reagents used were of guaranteed reagent grade. The use of glasswares, the most potential sources of external aluminium contamination, were avoided. Teflon wares were used throughout the study instead. The manipulation was carried out in a Class 10 clean bench.

Procedure. The water samples were acidified by the addition of 17 cm^3 of 6 mol dm^{-3} hydrochloric acid per 1 dm^3 immediately after sampling. To a 15 cm^3 aliquot of the sample taken in a Teflon beaker, 2 cm^3 of the DHAB solution was added. Then, 3 mol dm^{-3} potassium hydroxide was added dropwise until the brown color of DHAB (HL^-) was developed to neutralize the hydrochloric acid present. After the addition of 1 cm^3 of the butter solution (0.1 mol dm^{-3} THMAM-HCl, pH 8.0), the solution was heated for 20 min in a water bath at 70 °C and diluted to 25 cm^3 with water. An aliquot of the solution was injected to the HPLC with a 0.1 cm^3 loop injector. The detection wavelength was set at 510 nm, at which the maximum absorbance is obtained for the aluminium chelate ($[AlL_2]^-$).

Results and Discussion

A typical chromatogram for water analysis is shown in Fig. 1. The DHAB chelates of Al^{III} and Fe^{III} ions, and the excess reagent gave the well resolved peaks. Although V^{V} and Co^{II} ions may also give the eluted peaks in this system as was shown previously,[6] neither of them was detected in the water samples studied due to their lower concentrations. Iron(III) ion gives no significant effects up to 5 mg dm^{-3}, which is 100—1000 times greater

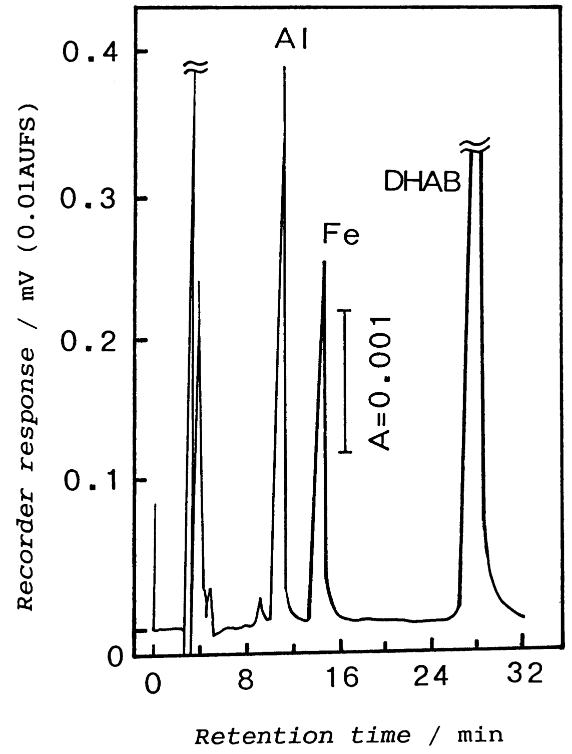

Fig. 1. Typical chromatogram for aluminium in natural water. Sample: ground water (Al: 11.5 μg dm^{-3}); DHAB: 8×10^{-5} mol dm^{-3}; Mobile phase: 61.7 wt% MeOH, Tetrabutylammonium bromide 6×10^{-3} mol kg^{-1}, EDTA 10^{-4} mol kg^{-1}, Tris(hydroxymethyl-amino)methane 0.002 mol kg^{-1} (pH 8.0); Flow rate 0.5 cm^3 min^{-1}; Column: LiChroCART RP-18; Detection wavelength: 510 nm.

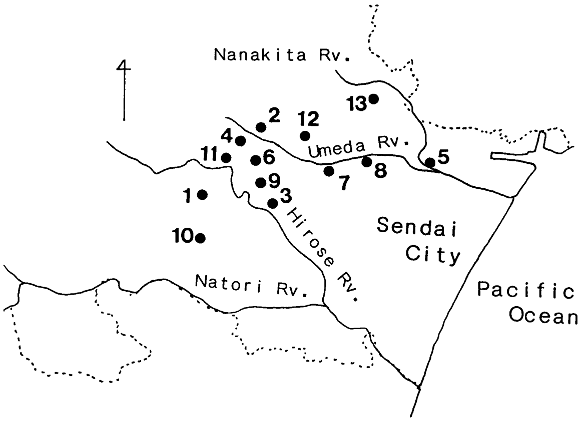

Fig. 2. Sampling location of ground water.

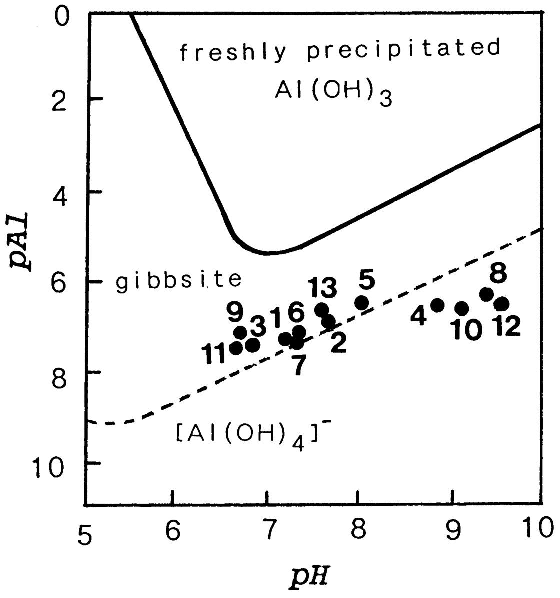

Fig. 3. Relationship between pH and aluminium concentration of ground water. Sampling date: Dec., 1989, *pAl*=−log ([Al]/mol dm^{-3}).

than those normally found in natural waters. Since the other metal ions essentially give no eluted peaks as mentioned above, none of them has any effect on the signal of aluminium.

The detection limit in pure solution, defined as twice the standard deviation of the blank signal, is 0.2 μg dm^{-3}. When this method is applied to water sample, the practical detection limit, defined as twice the standard deviation of the blank signal throughout the manipulation, is 1 μg dm^{-3} in water sample. The blank value is normally equivalent to less than 2 μg dm^{-3}. The sensitivity is limited by the blank contribution from the reagents used. Analyses of trace aluminium during the last decade have demonstrated the importance of avoiding contamination. Precautions to prevent contamination during sample handling and the choice of containers and reagents are very important, as described in our previous study.[10)]

The peak height calibration curve is linear up to 20 μg dm^{-3} at 0.01 absorbance unit full scale (AUFS). Examination for ground water samlple showed a coefficient of variation of 2.2% with the four replicate analyses at 7.6 μg dm^{-3}.

The analytical results of sea water and river water are showm in Table 1. To evaluate the effects of matrix of natural water, known amounts of aluminium were added to each sea water sample and then the analysis was carried out in the usual way. The recoveries shown in Table 1 confirms that there were no problems due to the matrix effects. Quantitative recoveries were also obtained for ground water samples. The ground waters collected from the thirteen wells in Sendai City (Fig. 2) were analyzed for aluminium. The depths of the wells were 30—200 m. The aluminium contents varied from 1.1 to 11.8 μg dm^{-3}. The relationship between aluminium concentration and pH shown in Fig. 3 suggests that the aluminium concentrations of the ground waters are close to the solubility curve of gibbsite (Al(OH)$_3$). Further, the alteration of the ground waters shown in Fig. 4 provides a check on the validity of the strong dependence of aluminium concentration on pH described above. It is generally accepted that pH of natural water increases as a result of water–mineral interaction. The pH value of ground water is also responsible for rainfall: A decreasing

Table 1. Analytical Results of Sea and River Waters

Sample	pH	Al added μg dm^{-3}	Al found μg dm^{-3}	Recovery %
Coastal seawater A	8.18	—	44.1	—
		67.6	114	103
Coastal seawater B	8.24	—	72.8	—
		67.6	135	92.0
Natori river	8.77	—	130	—
Hirose river	7.70	—	79.2	—
Umeda river	8.82	—	102	—
Nanakita river	7.70	—	39.5	—

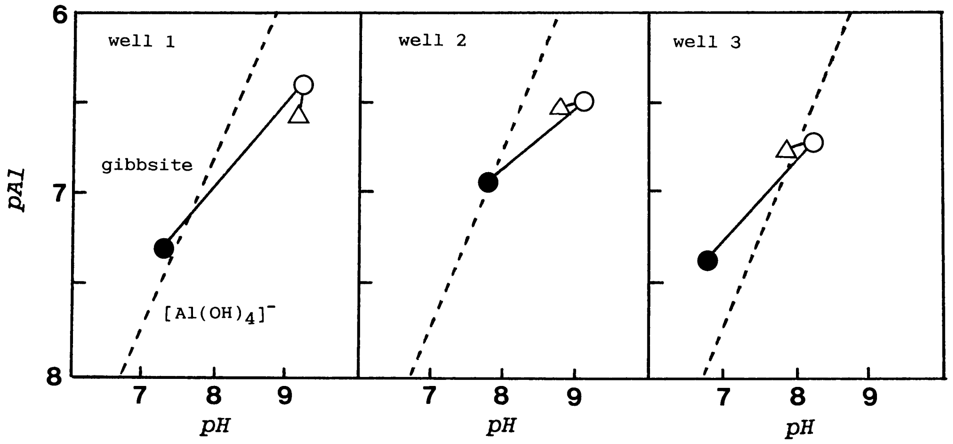

Fig. 4. Alteration of pH and aluminium concentration of ground water. Sampling date △: Mar., 1984, ○: Feb., 1985, ●: Dec., 1989.

rainfall results in an increase in pH and vice versa. Thus, the interaction between water and mineral, especially gibbsite, leads to the response of the aluminium concentration to alterations of pH of ground water.

We believe that the simple, sensitive, and reliable analysis by the proposed method can provide valuable informations on the behavior of aluminium in natural waters, which is as yet poorly understood.

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