

Determination of Trace Levels of Aluminum by Capillary Electrophoresis with Lumogallion Fluorometric Detection

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Abstract

The determination of aluminum in water samples is performed with capillary electrophoresis after a convenient preconcentration procedure involving simple evaporation and subsequent filtration. By using a fluorescence detector, a detection limit lower than 20 $\mu\text{g/L}$ aluminum is readily obtained. Only one peak from the aluminum–lumogallion complex is observed, which indicates the elimination of interference from foreign ions and lumogallion.

Introduction

Although aluminum was thought to be relatively harmless, evidence is increasingly implicating it in human disorders. Moreover, aluminum can be leached from sediments and soils and can pass into groundwater and surface water. Aluminum is also believed to be toxic to fish, other aquatic organisms, and several plant species (1). Due to its low solubility, the typical levels for aluminum concentration in natural waters are only 0.5–10 $\mu\text{g/L}$ in sea water (2) and 10–400 $\mu\text{g/L}$ in fresh and river water (3–5). With such a low concentration in natural water, sensitive analytical procedures are needed. A heated graphite furnace can be used because of its high sensitivity down to a few micrograms per liter (6) and relatively interference-free characteristics. One of the drawbacks of this method is that chloride causes low recoveries because of the volatility of aluminum chloride. Other sensitive techniques that have been proposed for the determination of aluminum include fluorometric (7–9) and electroanalytical (10–13) methods. However, electroanalytical methods are not widely applicable due to their lack of suitable electrophores. Lumogallion fluorometric analysis has gained widespread acceptance because of its high sensitivity and fewer interferences from foreign ions and other substances. Lumogallion was initially applied to aluminum complexation in 1968, and methods were then proposed for the determination of aluminum in sea water (14).

In recent years, there has been growing interest among

analytical chemists to exploit the high separation efficiency and instrumental simplicity for environmental analysis (15,16). However, to our knowledge, there has been no report to date on the determination of trace levels of aluminum in water by capillary electrophoresis (CE). In this paper, the determination of aluminum in water samples was performed by detection of the fluorescence from aluminum–lumogallion complex after it had been separated from potential interferences by using CE. The results were quite close to those obtained by using inductively coupled plasma–mass spectrophotometry (ICP–MS).

Experimental

Apparatus

A fused-silica capillary (50-cm effective length, 50- μm i.d.) obtained from Polymicro Technologies (Phoenix, AZ) was used for the separation. Detection of aluminum was carried out on a Shimadzu (Kyoto, Japan) model RF-535 fluorescence detector. A Shimadzu model RF-5000 spectrofluorophotometer was used to measure the fluorescence spectra. The detector cells were modified as follows: the on-column microfluorescence flow cell was fabricated by replacing the quartz cell with a separating capillary tube. A section of the polyimide coating on the capillary (approximately 5 mm) was removed to form the detection windows. A high-voltage power supply capable of delivering up to 15 kV was used. An ASO-1601 data acquisition system (Kenda, Singapore) was used to record the electrophoregrams on an IBM-compatible computer. For comparison of the results, a Perkin-Elmer Elan 5000 ICP–MS was used under the following operating parameters: RF power, 1.0 kW; plasma gas flow rate, 14.0 L/min; auxiliary gas flow rate, 0.80 L/min; sampling gas flow rate, 0.83 L/min; peristaltic pump flow rate, 1.0 mL/min.

Chemicals

All chemicals were of analytical-reagent grade or better. The stock solution of aluminum (1000 ppm) was prepared by dissolving $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (Fisher Scientific, Fair Lawn, NJ)

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into water. Lumogallion (formula weight = 344.73) (TCI, Tokyo, Japan) was prepared as a 0.1% solution in Millipore (Molsheim, France) water. Buffer solutions were prepared by mixing HAc with NH_4Ac to give a final concentration of 40mM HAc and 10mM NH_4Ac . The pH of the buffer was 4.0.

The sample solution was introduced manually by gravity feed. This was carried out by placing the tip of the capillary at the high-potential end in a sample vial at a height 15 cm higher than the buffer reservoir. The time for each injection was 10 s.

Methods

To one of four 5-mL volumetric flasks, 0.25 mL lumogallion (1000 ppm) and 0.2 mL sample were added. To each of the rest

of the volumetric flask, the above solutions and different amounts of standard aluminum solutions were introduced. Then the four volumetric flasks were filled with buffer to the mark, heated in boiling water for 15 min, and then allowed to cool down. The capillary was rinsed with buffer for 15 min by applying a pressure of 2 bar. The detector was allowed to warm up for 30 min before use. The excitation wavelength was set to 491 nm, and the emission wavelength was set to 576 nm. After sample introduction, the high-voltage power supply was turned on, and at the same time, the computer was started to record the chromatogram.

Results and Discussion

Figure 1 shows electrophoregrams of the sample solution containing lumogallion and variable aluminum concentrations. As shown in Figure 1, only one peak was observed, which demonstrated that the interference from lumogallion that is normally presented in HPLC (17) had been eliminated. The elimination may have resulted from the negative charge on lumogallion, which prevented it from moving toward the low potential end of the capillary.

Effect of pH

The fluorescence intensity of the aluminum–lumogallion complex was measured over a range of pH conditions from 3.55 to 4.63 (Figure 2). The peak height did not change significantly over the range studied. The optimal pH condition was selected as 4.0 due to the slightly

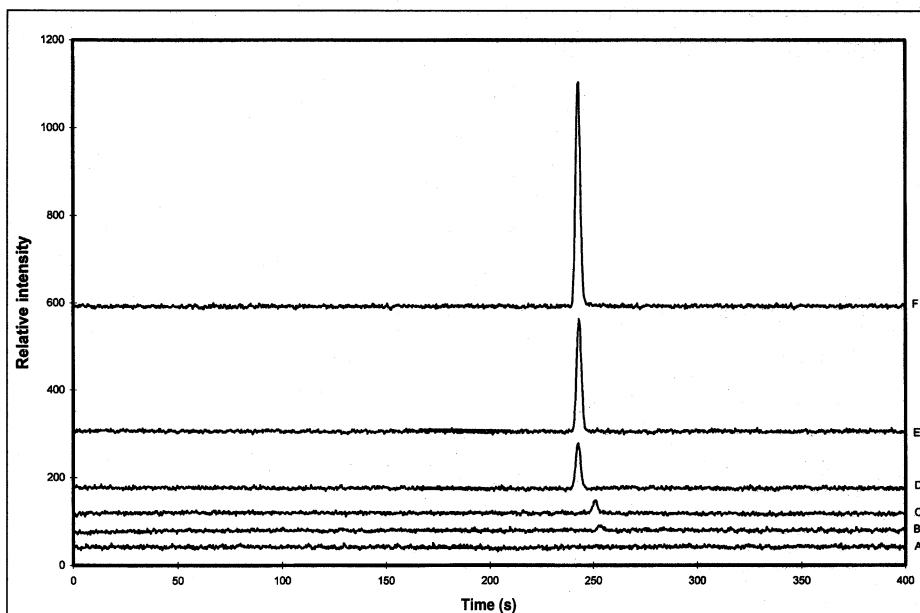


Figure 1. Chromatograms of the aluminum–lumogallion complex with variable aluminum concentrations. Lumogallion, 50 ppm; aluminum, (A) 0 ppb, (B) 200 ppb, (C) 400 ppb, and (D) 1000 ppb. Capillary inner diameter, 75 μm ; buffer, pH 4.0 (40mM HAc, 10mM NH_4Ac); voltage, 15 kV; excitation wavelength, 491 nm; emission wavelength, 576 nm; sampling time, 10 s. Intensity is in relative units.

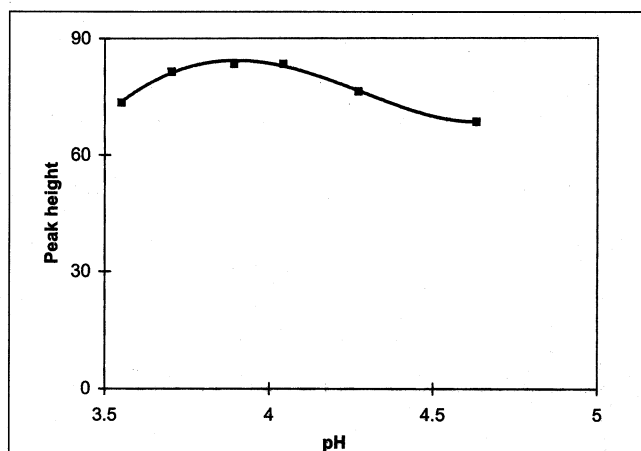


Figure 2. Effect of pH on the fluorescence intensity obtained from a 4-ppm aluminum solution. Peak height is in relative units. Other conditions are given in Figure 1.

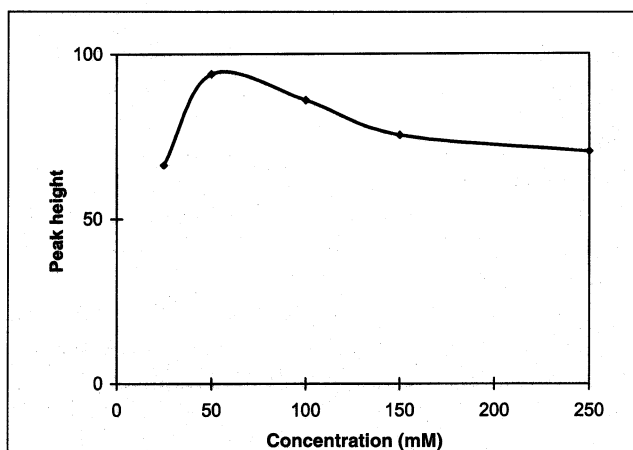


Figure 3. Variation of fluorescence intensity with ionic strength. pH = 4.0. Other conditions are given in Figure 1.

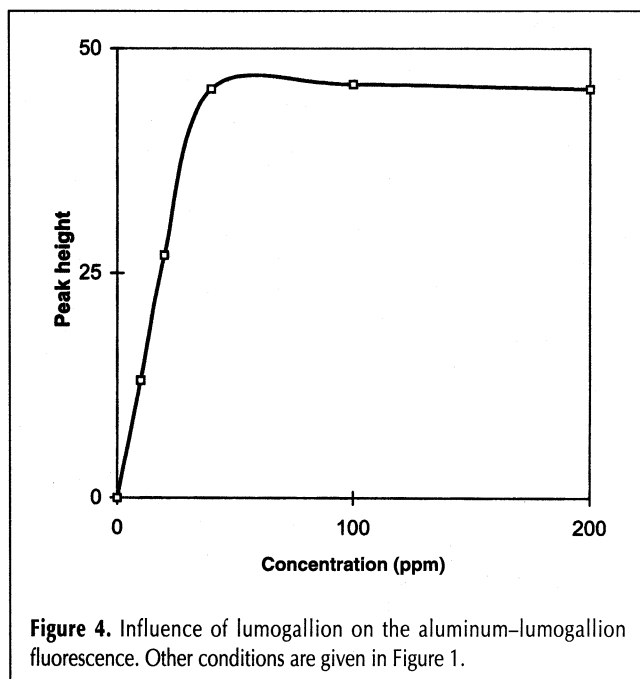


Figure 4. Influence of lumogallion on the aluminum-lumogallion fluorescence. Other conditions are given in Figure 1.

larger peak heights obtained and was used in subsequent experiments.

Effect of ionic strength

The pH was fixed at 4.0, and the effect of ionic strength was investigated over the range of 25–250mM. The maximum intensity was obtained in the 50mM buffer solution (Figure 3). Therefore, the 50mM buffer (consisting of 40mM HAc and 10mM NH_4Ac) was selected and used in subsequent experiments.

Effect of lumogallion concentration

The effect of lumogallion concentration on the peak height was also investigated. The results are shown in Figure 4. The peak height ceased to increase after the concentration of lumogallion exceeded 40–50 ppm. The optimal concentration of lumogallion was selected to be 50 ppm.

Interferences

No peaks were observed for solutions containing lumogallion and any of the following ions, which are common in natural waters: Fe^{3+} , Ca^{2+} , Mg^{2+} , Cu^{2+} , and Zn^{2+} ; all were at concentration of 10 ppm. Therefore, this method can be very selective for the determination of aluminum in natural waters.

Precision and accuracy

The peak height was found to increase linearly with an increase of aluminum concentration in the range of 40–2000 ppb. The linear equation for the calibration curve is:

$$\text{Peak height} = 3.9 + 0.25 \times C_{\text{Al}}$$

The correlation coefficient was 1.000. The curve bends after the upper detection limit. The detection limit was calculated to be 19 ppb based on 3 standard deviations from nine repetitive runs at 100 ppb aluminum concentration. The relative standard deviation (RSD) in peak height at 100 ppb was 3.1%.

The recoveries for 200 ppb aluminum added to three different water samples (river water, reservoir water, and spring water) were 94, 104, and 95%, respectively.

Application to water samples

The above method was used for the determination of aluminum in several water samples, including water collected from a river (Bukit Timah River, Singapore), a reservoir (Thomson Reservoir, Singapore), and spring water (Indonesia). The samples were pretreated with the following procedures: 50 μL super-pure HCl was added to a 300-mL filtered water

Sample source	River		Reservoir		Spring water	
	Content (ppb)	RSD (%)	Content (ppb)	RSD (%)	Content (ppb)	RSD (%)
CE	87	9.6	38	6.6	83	8.8
ICP-MS	104	1.6	50	2.9	99	1.5

* For CE, RSD was calculated from three injections; for ICP-MS, RSD was calculated from three replicates.

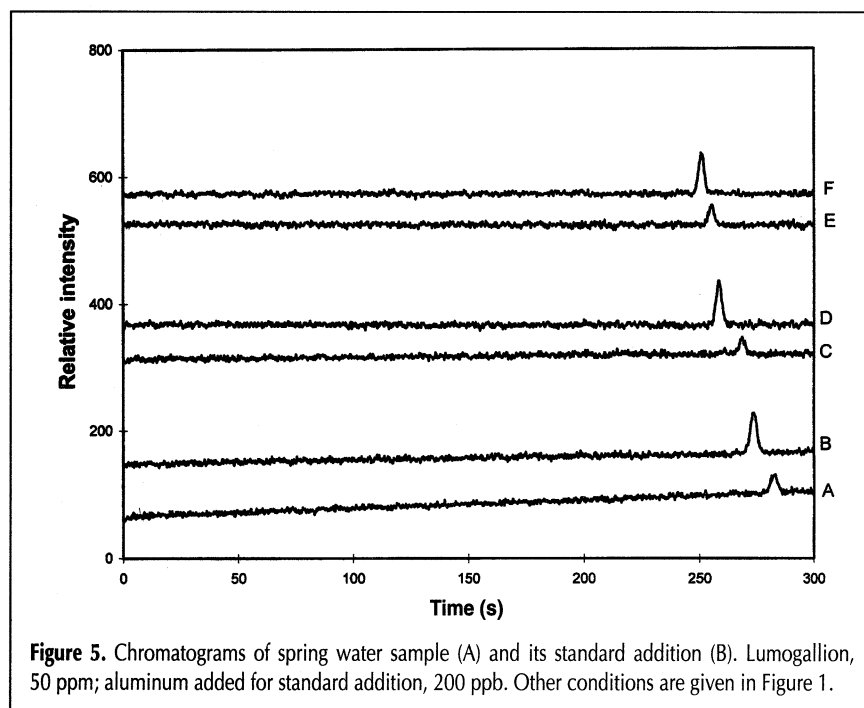


Figure 5. Chromatograms of spring water sample (A) and its standard addition (B). Lumogallion, 50 ppm; aluminum added for standard addition, 200 ppb. Other conditions are given in Figure 1.

sample to prevent aluminum precipitation. The solution was allowed to evaporate to approximately 5 mL, and after filtering, it was diluted to 10 mL with Millipore water before analysis by CE. For comparison, ICP-MS analysis was performed on the same samples. Each result was obtained from three repetitive measurements. The results and RSDs are indicated in Table I, and the electrophoregrams for the spring water sample are shown in Figure 5.

The results obtained by using the ICP-MS method were quite close to those obtained by CE although those obtained through ICP-MS were slightly higher. One of the possible reasons is that the ICP-MS method determines the total concentration of aluminum in the sample whereas CE determines only those in the ionic state.

Acknowledgment

Financial support of this study by the National University of Singapore is gratefully acknowledged.

References

1. J.W. Robinson and P.M. Deano. Acid rain: The effects of pH, aluminum, and leaf decomposition products on fish survival. *Am. Lab.* **18**: 17-26 (1986).
2. B. Mason. *Principles of Geochemistry*. John Wiley & Sons, New York, NY, 1966, p. 195.
3. A.A. Levinson. *Introduction to Exploration Geochemistry*, 2nd ed. Applied Publishing, Wilmette, IL, 1980.
4. J.D. Hem, C.E. Roberson, C.J. Lind, and W.L. Polzer. *U.S. Geological Survey, Water Supply Paper*, 1973, p. 1827E.
5. T.S. West and H.W. Nurnberg. *The Determination of Trace Metals in Natural Waters*. Blackwell Scientific Publications, Washington, DC, 1992.
6. K.E. Johnson, A.K. Brichta, and K.-L. Holter. Trace analysis for aluminum by furnace atomic absorption spectroscopy and differential pulse polarography. *Can. J. Chem.* **66**(1): 139-42 (1988).
7. M.S. Shuman. Dissociation pathways and species distribution of aluminum bound to an aquatic fulvic acid. *Environ. Sci. Technol.* **26**(3): 593-98 (1992).
8. K.R. Vitense and L.B. McGown. Simultaneous determination of aluminum(III) and gallium(III) with lumogallion by phase-resolved fluorimetry. *Analyst* **112**(9): 1273-77 (1987).
9. A.G. Howard, A.J. Coxhead, I.A. Potter, and A.P. Watt. Determination of dissolved aluminum by the micelle-enhanced fluorescence of its lumogallion complex. *Analyst* **111**(12): 1379-82 (1986).
10. K.E. Johnson and R.G. Treble. Determination of aluminum in human cerebrospinal fluid through the electrochemical and spectroscopic properties of its complex formed with solochrome violet RS. *Can. J. Chem.* **71**(6): 824-26 (1993).
11. T.M. Florence, F.J. Miller, and H.E. Zittel. Voltammetric determination of aluminum by oxidation of its solochrome violet RS complex at the rotated pyrolytic graphite electrode. *Anal. Chem.* **38**(8): 1065-67 (1966).
12. G.S.P. Ritchie and A.M. Posner. The determination of trace levels of aluminum by differential pulse polarography. *Anal. Chim. Acta* **117**: 233-39 (1980).
13. H.H. Willard and J.A. Dean. Polarographic determination of aluminum. *Anal. Chem.* **22**(10): 1264-67 (1950).
14. D.J. Hydes and P.S. Liss. Fluorimetric method for the determination of low concentrations of dissolved aluminum in natural waters. *Analyst* **101**: 922-31 (1976).
15. J.W. Jorgenson and K. Lukacs. Zone electrophoresis in open-tubular glass capillaries. *Anal. Chem.* **53**: 1298-1302 (1981).
16. S. Terabe, K. Otsuka, K. Ichikawa, A. Tsuchiya, and T. Ando. Electrokinetic separations with micellar solutions and open-tubular capillaries. *Anal. Chem.* **56**: 111-13 (1984).
17. J. Wu, C.Y. Zhou, H. Chi, M.K. Wong, H.K. Lee, H.Y. Ong, and C.N. Ong. Determination of serum aluminum using an ion-pair reversed-phase high-performance liquid chromatographic-fluorimetric system with lumogallion. *J. Chromatogr. B* **663**: 247-53 (1995).

Manuscript accepted March 6, 1997.