

Determination of Ionic Aluminum Concentrations in Fresh Waters by Adsorptive Stripping Voltammetry Using DASA*

Shuping Bi

Chemistry Department and State Pilot Lab of Coast & Island Exploitation, Nanjing University, Nanjing, 210093, P.R.China

Abstract: *Application of the adsorptive stripping voltammetry using DASA (1, 2-dihydroxyanthraquinone-3-sulfonic acid) in the buffer solution of triethanolamine (pH 7.6) to determine the ionic forms of aluminum in fresh waters were presented in this paper. No serious interferences from Zn, Fe, Cl and V were found. Small amounts of Ca enhanced the analytical signal. Electroactive or ionic aluminum concentrations in fresh waters sampled both from China and USA was analysed.*

Keywords: *Ionic aluminum concentration, Fresh waters, Speciation, Adsorptive stripping voltammetry*

1. Introduction

The ecological effect of aluminum is an attractive subject facing to environmental scientists at present (Sposito., 1989). Acid rain caused dissolution of aluminum from the soil and resulted in the elevation of Al concentrations in the surface waters. Increased Al concentrations are toxic to plants and aquatic organisms including fishes (Correll *et al.*, 1987). Aluminum concentrations in freshwaters are generally at ppb levels. The toxicity of aluminum depends on its forms present in the water. Inorganic complexes of aluminum are thought to be more toxic than organic complexes. Therefore, it is critical to determine ionic aluminum concentrations rather than its total concentration in the fresh waters. As an alternative characterization of electroactive Al which might be susceptible to direct measurement, adsorptive stripping voltammetry (ASV) using SVRS or PCV has been employed for determining ionic Al in surface waters in recent years (Johnson *et al.*, 1988 & Vukomanovic *et al.*, 1991). In this paper, we report the application of ASV measurement of ionic Al in fresh waters using DASA in the buffer solution of triethanolamine. It overcomes the drawback of suffering Zn interference in the BES buffer solution proposed by Van den Berg. *et al.* (1986). Fresh water samples collected both from the eastern areas of China and USA were analysed and the results were compared with those obtained by GF/AAS method.

* Received 1997-02-25; accepted 1998-03-27.

2. Experiment

Chemicals Analytical-reagent grade chemicals and de-ionized water from Cartridge system (HN Ultrapure W/O DYE, Barnstead Thermolyne, USA) were used to make solutions. The Al standard stock solution of $0.54 \text{ g}\cdot\text{L}^{-1}$ was prepared by dissolving an appropriate amount of high-pure Al metal powder in 1:1 HCl, then transferring it to a 250 ml flask and diluted it to the mark with water. Baker analysed reagent 1 000 ppm Al (atomic spectral standard, J.T. Baker Chemical Co.,) was also used. The standard solutions were obtained by diluting the stock solution with water. A $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ solution of DASA was prepared by dissolving an appropriate amount of Alizarin Red S (Fluka Chemical Inc.) in water. Buffering solution was prepared by addition of the 100 ml 1:1 HCl to 100 ml solution of triethanolamine (1:4), then was partially neutralized with $1 \text{ mol}\cdot\text{L}^{-1} \text{ NH}_3\cdot\text{H}_2\text{O}$ to pH 7.6.

2.1 Apparatus

An ASD-1 type electrochemical analyser (Shangdong Seventh Electric Factory, China) or a BAS-CV-1B-1200 cyclic voltamograph (BAS Inc, USA) was used throughout the experimental. The working electrode was a hanging mercury drop electrode (GHJ-3A HMDE, Chemistry Department, Shandong University, China). The surface of the HMDE was 0.0258 cm^2 . The reference electrode was saturated calomel and the counter electrode was a platinum foil. pH was measured with a PXD-12 pH meter (JiansuElectroanalysis Factory, China) or a digital pH meter (Cole-Parmer Instrument Co. USA). A Model 79-1 magnetic stirrer (Jiangsu Jintan Guohua Instrumentation Factory) and a stirring bar provided the convective transport during the accumulation step. The adsorptive stripping voltammograms were recorded using a type 3086-11 X-Y recorder (Hokushu Electric Co., Yokogama, Japan). Potentials were quoted relative to the saturated calomel SCE.

2.2 Procedure

A volume of water sample was pipetted into the polarographic cell. 1.5 ml of $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ DASA and 1.5 ml of triethanolamine buffer solution were added to the cell, giving $5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ DASA and $0.033 \text{ mol}\cdot\text{L}^{-1}$ triethanolamine buffer solution of pH 7.6. Then the solution was made up the total volume to 30 ml with water. The aluminum concentration present in the final polarographic solution should not exceed $30 \mu\text{g}\cdot\text{L}^{-1}$. After deaerating the solution with pure nitrogen for 10 min, the stirrer was started. A new mercury drop was then extruded which signifies the beginning of the adsorption time. The accumulation potential - 0.61 V was applied to the HMDE while the solution was stirred for 60 s. The stirring was stopped and after 10 s of quiescent time, the voltam-mogram was recorded by applying a negative linear scan at $100 \text{ mV}\cdot\text{s}^{-1}$. The aluminum in the sample was evaluated from a repeated measurement after a standard addition.

3. Results and discussions

Fig. 1(not shown) shows that DASA in the triethanolamine buffer solution gives reduction peak P_1 at - 0.60 V. Adding of aluminum produces a new peak P_2 at - 0.72 V representing the reduction of Al-DASA complex. Under the optimal conditions (5×10^{-5} mol·L⁻¹ DASA, 0.033 mol·L⁻¹ triethanolamine buffer solution of pH 7.6, accumulation potential - 0.61 V and accumulation time 60 s), this P_2 peak height is proportional to the aluminum concentrations and can be quantitatively used in analysis of aluminum. The linear working range used in our test is 3 – 30 ppb.

The possible interferences of foreign ions on the detection of aluminum in fresh waters were tested. As shown in Tab. 1, there was no serious interfering species were found, since the amounts of most foreign ions present in the fresh waters were very low compared with that of aluminum (Lewis, 1989). Interferences from Fe, Cl, V and Zn were not found either, which were reported by the literatures when using SVRS (Johnson *et al.*, 1988), PCV (Vukomanovic *et al.*, 1991) and DASA in BES buffer solution (Van Den Berg *et al.*, 1986). Similar to the phenomenon observed in the BES buffer solution (Vilchez *et al.*, 1993), adding Ca (II) in the test solution might increase the peak height of Al-DASA complex. Fig. 2 indicates that the calcium in the fresh waters could enhance the determination of aluminum provided that the Ca/Al is smaller than 400. Behind Ca/Al > 400, a procedure of removing calcium described in the literature (Wang *et al.*, 1986) is necessary.

The proposed method was applied to the determination of Al in real water samples. The fresh waters were collected both from China and U.S.A. The sampling areas are described as following:

Tab. 1 Interferences of foreign ions (27 ppb Al)

TR	Foreign Ions
10	Li(I), V(V), Ni(II), Bi(III), Cr(IV)
20	In(III), Mo(VI), La(III), Mn(VII)
50	Zr(IV), Co(II), Ga(III)
120	Mn(II), Cu(II), Zn(II), Fe(III), Ce(IV), EDTA
250	Mg(II), Ba(II), Sn(II), Cd(II)
500	Tl(I), Hg(II), Citrate
700	Ge(IV), Phosphate
>1000	Na(I), K(I), Cl ⁻ , NO ₃ ⁻ , NO ₂ ⁻ , SO ₄ ²⁻ , F ⁻ , I ⁻ , Tartrate, Silicate

Tab. 2. Results of determining Al in water samples (ppb)

Samples	This method	GF/AAS
USA, 1996.8		
S1	18.0 ± 1.5	18
S2	26.0 ± 1.7	27
S3	90.0 ± 8.1	98
S4	183 ± 14	203
S5	24.0 ± 2.2	24
S6	151 ± 12	155
China, 1995.5		
S7	156 ± 14	150
S8	189 ± 17	190
S9	59.4 ± 6.0	150
S10	63.4 ± 6.0	160

USA: Stream waters (S1-S5) sampled from Conestoga River Cluster and Buffalo Creek Cluster, the Chesapeake Bay Survey Spot Sampling Stations. S6 was the rainwater sampled in Edgewater, Maryland. The Ca/Al ratios in these waters were below 400.

China: Fresh waters sampled from Nanjing, a city of the eastern area of China. In which,

S7: tap water drawn from the local water supplies;

S8: river water from Yang-Zi-Jiang, the longest river in China;

S9: river water from Qing-Huai-He, a small river around Nanjing;

S10: lake water from Xuan-Wu lake, a park in the centre of Nanjing.

Calcium was removed prior to the voltammetric determination since the Ca/Al ratios in those waters are exceed 400.

Tab. 2 brings the results of determining ionic aluminum in these fresh waters by the proposed approach. They were compared with the results obtained by GF/AAS method. As shown in Tab. 2, almost all of the Al found by GF/AAS in samples S1-S8, were electroactive (more than 90 %). In contrast, only some of that in S9 and S10 samples responded to ASV. This indicates that in these waters the most parts of aluminum were bound with organic legends and only 40 % aluminum are electroactive or in the ionic forms. The result is reasonable because the waters S1-S8 are clean with the DOC values lower than $2 \text{ mg}\cdot\text{l}^{-1}$, whereas S9 & S10 suffered serious organic pollution due to the rich nourishment and industrial drainage.

In conclusion, the proposed method provides a simple and convenient approach to the measurement of ionic Al in fresh waters. Such use of DASA in the buffer solution of triethanolamine offers an alternative ASV scheme that compares favourably with the use of other ligands for the same task.

Acknowledgements

This project is supported by the Research Funding of Electrochemistry Open Laboratory of Changchun Applied Chemistry Institute, Chinese Science Academy, National Natural Science Foundation of China No. 29777013 and Jiangsu Province, Fok Ying Tung Education Foundation of Hong Kong and Visiting Fellowship of SERC of USA. Great attitudes are given to Prof. Hongjun Jin, Dayuang Yang, Rongshi Cheng, Hongyuan Chen and Director of SERC, D.L. Correll for their supports. The author also thanks Joe Miklas, Bob O'Meally and the Modern Analytical Center of Nanjing University for their assistances for measurements of DOC and

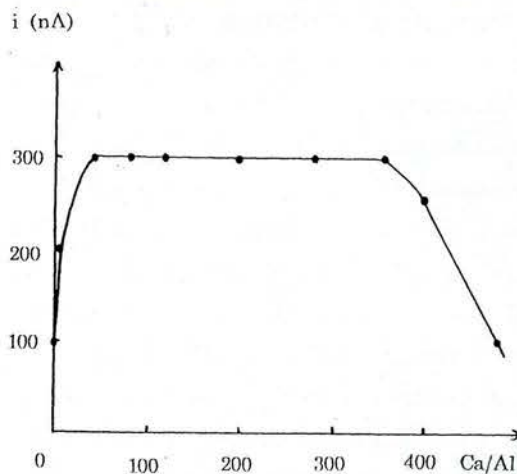


Fig. 2 Influence of Ca/Al ratio on analytical signal (10 ppb Al, other condition as Fig. 1)

aluminum in water samples by GF/AAS method. Part of this work is also supported by the funding from Nanjing Municipality Government.

References

- Correll, D. L., Miklas, J. J., Hines, A. H., and Schafer, J. J. 1987. Chemical and biological trends associated with acidic atmospheric deposition in the Rhode River watershed and estuary. *Water Air Soil Pollut.* 35: 63-86.
- Hernande-Brito, J. J., Gelado-Caballero, M. D. and Perez-Pefia, J. 1994. Fast determination of aluminum reactive to 1,2-dihydroxy-anthraquinone-3-sulfonic acid in sea water. *Analyst.* 119: 1593-1597.
- Johnson, K. E., Brichta, A. K. and Holter, K. L. 1988. Trace analysis for aluminum by furnace atomic absorption spectroscopy and differential pulse polarography. *Can.J.Chem.* 66: 139-142.
- Lewis, T. E. 1989. *Chemistry and Toxicology of Aluminum*, Lewis Publishers, Inc, Michigan.
- Sposito, G. 1989. *The environmental chemistry of aluminum*, CRC Press, Inc, Boca Raton, Florida.
- Van Den Berg, C. M. G., Murphy, K., and Riley, J. P. 1986. The determination of aluminum in seawater and fresh water by cathodic stripping voltammetry. *Anal.Chim.Acta.* 188: 177-185.
- Vukomanovic, D. V., Page, J. A. and Vanloon, G. W. 1991. Voltammetric determination of Al(III) with adsorptive preconcentration of the pyrocatechol violet complex. *Can.J.Chem.* 69: 1418-1426.
- Wang, L. Z., Chen, R. L., Wen, S. Q. and Zhu, J. R. 1986. Voltammetry study of aluminum of Al-alizarin S adsorptive complex. *Chinese J. of Anal Chem.* 15: 118-122