A.C. OSCILLOPOLAROGRAPHIC DETERMINATION OF ALUMINUM IN NATURAL AND DRINKING WATERS USING THE ADSORPTION OF THE Al(III)-1,2-DIHYDROXYANTHRAQUINONE-3-SULFONIC ACID COMPLEX

Shuping BI[1] and Zhengjiang ZHANG[2]

Chemistry Department, Nanjing University, Nanjing, 210093, People's Republic of China;
e-mail: [1] bisp@netra.nju.edu.cn, [2] nucskac@netra.nju.edu.cn

Received April 25, 1996
Accepted August 19, 1996

This paper presents a very simple and rapid method for determination of aluminum in natural and drinking waters by using a.c. oscillopolarographic adsorptive wave of the Al(III)-1,2-dihydroxyanthraquinone-3-sulfonic acid complex in a triethanolamine buffer solution of pH 7.6 at HMDE. A linear dependence between the incision height on d*E*/d*t*–*E* oscillogram and the aluminum concentration was obtained in the range from $5 \cdot 10^{-6}$ to $5 \cdot 10^{-5}$ mol l^{-1}. The detection limit is $1 \cdot 10^{-6}$ mol l^{-1} and the relative standard deviation is 6.0% for $4 \cdot 10^{-5}$ mol l^{-1} aluminum. This method has the distinct advantages of cheap instrumentation, simple and rapid manipulation and deaeration is unnecessary. It is especially suitable for the fast determination of aluminum in natural and drinking water samples.

Key words: A.c. oscillopolarography; Aluminum; Natural and drinking waters; 1,2-Dihydroxyanthraquinone-3-sulfonic acid.

Aluminum is the most abundant metallic element in the earth crust. Determination of aqueous aluminum is of great significance environmentally, because of its link to human diseases and toxicity to plants[1,2]. Many available methods have been developed in the last two decades, such as, graphite furnace atomic absorption spectrometry (GFAAS), molecular fluorimetry (MF), inductively coupled plasma atomic emission spectrometry (ICP-AES), neutron activation (NA) and adsorption voltammetry (AV)[3,4]. These methods are very sensitive with the detection limit of 10^{-9} mol l^{-1}. However, there are still some problems existing for the application of these methods to practical water sample analysis, e.g. serious matrix effects (GFAAS), expansive instrumentation (ICP–AES and NA), very careful laboratory techniques and complicated manipulation (MF and AV). On the other hand, the aluminum concentration in natural and drinking waters generally falls in the range of 10^{-6}–10^{-4} mol l^{-1} (refs[5,6]). From the practical standpoint, we hope to develop a very simple and inexpensive method for determining aluminum in real water samples. In this paper, the focus will be on fast determination of aluminum in natural and drinking water samples with an emphasis on 10^{-6}–10^{-5} mol l^{-1} aluminum system.

A.c. oscillopolarography (ACOP) is a kind of current-controlled electrochemical method introduced by Heyrovsky[7,8]. It has been widely used in microanalysis and environmental monitoring[9–12]. The aim of this paper is to apply a.c. oscillopolarography to the determination of aluminum in natural and drinking waters using the adsorption of the Al(III)-1,2-dihydroxyanthraquinone-3-sulfonic acid complex.

EXPERIMENTAL

Instrumentation

The experimental setup for providing the ACOP oscillogram $dE/dt–E$ is similar to that described by Kalvoda[18]. We have modified this circuit by employing a three-electrode system[14,15]. A hanging mercury drop electrode (HMDE) served as the working electrode (A = 0.0302 cm^{-2}) and saturated calomel and platinum foil as reference and counter electrodes, respectively. The frequency of alternating current passed through the electrolytic cell is 50 Hz. The $dE/dt–E$ oscillogram was observed on a SR-8 oscillograph (Jiangsu Yangzhong Electronic Factory, China). An ASD-1 type electrochemical analyzer (Shandong Seventh Electric Communication Factory, China) was used to measure the pH value of solution and carry out the linear voltammetric experiment. A Model 79-1 magnetic stirrer (Jiansu Jingtan Guohua Instrumentation Factory, China) was used to stir the solution. The experiment was performed at 25 ± 0.2 °C.

Chemicals

Aluminum standard stock solution (0.2544 mol l^{-1}) was prepared by dissolving 3.4319 gram aluminum foil (spectrum pure) in about 250 ml of dilute HCl, then transferring the solution into a 500 ml calibrated flask and adjusting to volume with water. Adequate dilution was made before each experiment.

1,2-Dihydroxyanthraquinone-3-sulfonic acid (Alizarin S) solution (0.1 mol l^{-1}) was obtained by dissolving 3.6 g of Alizarin S in about 50 ml of water. The solution was transferred to 100 ml flask and then filled up with water.

A buffer solution of triethanolamine (pH 7.6) was prepared by adding 100 ml triethanolamine solution (1 : 4) to 100 ml of 1 mol l^{-1} HCl, and the pH was adjusted to 7.6 with 1 mol l^{-1} $NH_3 . H_2O$.

All chemicals were of analytical grade and the solutions were made by twice distilled water from quartz. All laboratory glassware and plasticware were acid washed and rinsed with water before each experiment. River and lake water samples were collected using 500 ml polyethylene bottles.

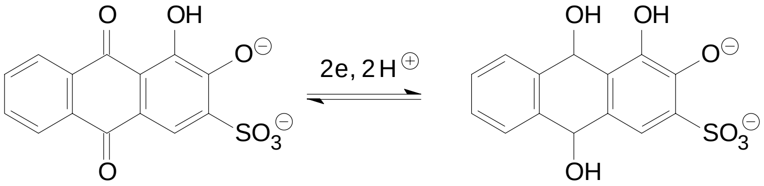
Procedures

Taking a certain amount of aluminum standard solution in electrolytic cell, adding 2.5 ml triethanolamine buffer solution, 2.5 g KCl and 1 ml Alizarin S, and then filling to the marked-level of 50 ml with water. After adjusting suitable electronic parameters and waiting for a 3 min rest period, the incision height $(dE/dt)_p$ is recorded. The sensitivity of the oscillograph is: $X(E)$ = 0.5 V cm^{-1} and Y (dE/dt) = 5 mV cm^{-1}.

RESULTS AND DISCUSSION

A.c. Oscillopolarograms of Alizarin S and Al–Alizarin S Complex

Figure 1 shows the a.c. oscillopolarograms of Alizarin S and Al–Alizarin S complex. In the system of pure base solution (triethanolamine buffer plus supporting electrolyte KCl) and Alizarin S, only a sharp peak P_1 (E_{P_1} = –0.74 V) was observed on the dE/dt–E oscillogram. It is due to the reversible adsorption reaction of Alizarin S on the mercury electrode surface. The electrode reaction[16–19] is:



(*A*)

In the presence of 1 . 10^{-6} mol l^{-1} aluminum, a new sharp peak P_2 appears at the potential of –0.85 V, which represents the complex wave of Al–Alizarin S. The electrode reaction obeys the following mechanisms[20].

$$\mathrm{Al^{3+} + (HL)^{2-} = AlL + H^+} \qquad \text{coordination reaction in solution} \qquad (B)$$

$$\mathrm{(HL)^{2-} = (HL')^{2-}_{ad}} \qquad \text{adsorption process of coordination agent} \qquad (C)$$

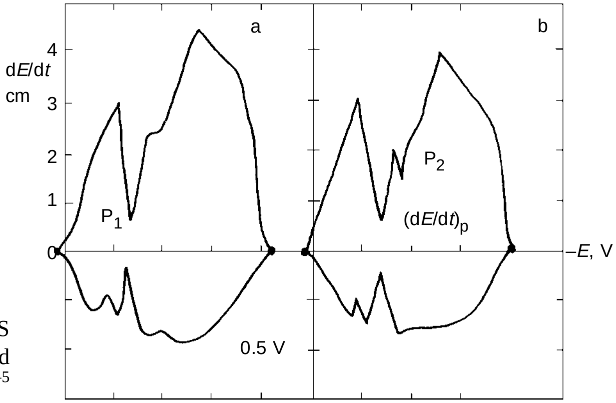


FIG. 1
A.c. oscillopolarograms of Alizarin S 1.6 . 10^{-3} mol l^{-1} (a), Alizarin S and Al–Alizarin S complex, c^*_{Al} = 1 . 10^{-5} mol l^{-1} (b)

$$\mathrm{AlL} + (\mathrm{HL})_{\mathrm{ad}}^{2-} = (\mathrm{AlL}_2)_{\mathrm{ad}}^{3-} + \mathrm{H}^+ \quad \text{induced adsorption process of coordination complex} \qquad (D)$$

$$(\mathrm{HL})_{\mathrm{ad}}^{2-} + 2\,\mathrm{e} + 2\,\mathrm{H}^+ = (\mathrm{HL}')_{\mathrm{ad}}^{2-} \quad \text{electrode reaction of coordination agent} \qquad (E)$$

$$(\mathrm{AL}_2)_{\mathrm{ad}}^{3-} + 4\,\mathrm{e} + 4\,\mathrm{H}^+ = (\mathrm{AlL}_2')^{3-} \quad \text{electrode reaction of coordination complex} \qquad (F)$$

The incision height $(\mathrm{d}E/\mathrm{d}t)_\mathrm{p}$ declines with the increase of aluminum concentration as a linear function and can be quantitatively used in aluminum determination.

Optimization of Experimental Conditions

The optimum experimental conditions for the determination of aluminum concentration were investigated and some results were obtained.

It is necessary to remove the dissolved oxygen in solution in ordinary adsorptive voltammetric determination of aluminum. Otherwise, the Al-organic adsorption wave will not appear on the *i*–*E* voltammogram, which is due to the influence of slow irreversible reduction of oxygen on the mercury electrode. However, under the condition of fast potential scan (0.02 s per cycle, f = 50 Hz) of ACOP, dissolved oxygen does not interfere with the electrode reaction of the Al–Alizarin S complex. The working curves for both cases are almost the same (see Fig. 2).

pH value of the solution is a critical parameter for determining Al. The incision height $(\mathrm{d}E/\mathrm{d}t)_\mathrm{p}$ is very sensitive to pH and achieves its minimum at pH 7.6. At pH

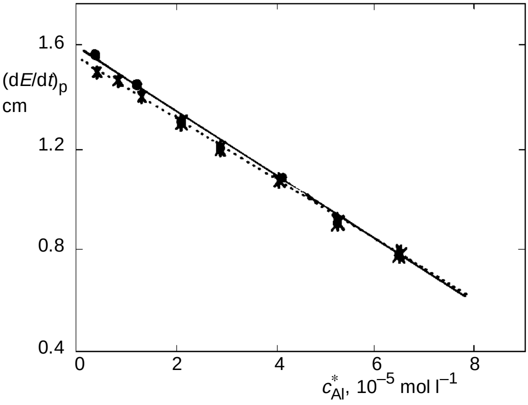


FIG. 2
Working curves for determinating aluminum in the presence of dissolved oxygen (———), after deaeration (· · · ·)

< 6.5 or > 8.5, the complex is not formed. Therefore, maintaining pH 7.6 is very important (see Fig. 3).

Figure 4 indicates that the amount of triethanolamine buffer solution used has a remarkable influence on $(dE/dt)_p$ and its linear working range. We choose 2–3 ml of triethanolamine buffer solution in our test.

The optimum Alizarin S concentration for minimum $(dE/dt)_p$ was $1.6 \cdot 10^{-3}$ mol l^{-1} (see Fig. 5).

We have tested many kinds of salts as the supporting electrolytes and found that KCl is the most suitable one, where the linear working range is longer than in other types of mediums (see Fig. 6). The suitable concentration of KCl used is 0.3–1.0 mol l^{-1}.

The Stability, Reproducibility, Detection Limit and Linear Working Range

The stability and reproducibility of this method for determining Al are excellent. For $4 \cdot 10^{-5}$ mol l^{-1} Al^{3+}, the incision height $(dE/dt)_p$ is 1.06 ± 0.05 cm in the period of

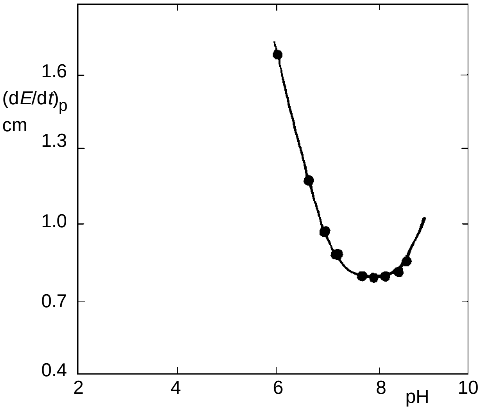


FIG. 3
$(dE/dt)_p$ vs pH for $6.2 \cdot 10^{-5}$ mol l^{-1} Al^{3+}

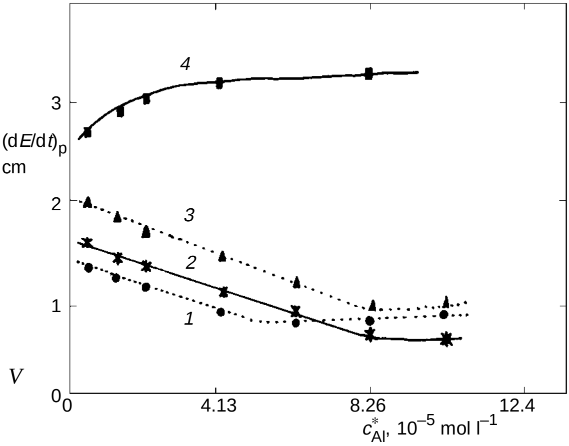


FIG. 4
Influences of amount of triethanolamine V (ml): (*1*) 1, (*2*) 2, (*3*) 3, (*4*) 4

60 min and the relative standard deviation is 6.0% ($n = 10$). The detection limit of this method is 1 . 10^{-6} mol l^{-1} and the linear working range is 5 . 10^{-6}–5 . 10^{-5} mol l^{-1}.

Interferences by Foreign Ions

The interference by foreign ions was investigated. Table I indicates that the most seriously interfering ions in natural waters are Ca^{2+} (Ca forms complicated complex with Al and Alizarin S at pH 7.6 (ref.[21], see Fig. 7), and dissolved organic substances (citrate, tartrate, etc.). The former can be removed by precipitation with carbonate[22] and the latter may be destroyed by UV-light oxidation method[23].

TABLE I
Interferences by various foreign ions

The maximum tolerance c^*_M/c^*_{Al}	c^*_M, mol l^{-1}	Ions
1	3.0 . 10^{-5}	Zn^{2+}, Cu^{2+}, Bi^{3+}, MnO_4^-, $Cr_2O_7^{2-}$
5	1.5 . 10^{-4}	In^{3+}, Ni^{2+}, Li^+, Mo(VI), Ba^{2+}, Sn^{2+}, La^{3+}, Ga^{3+}
10	3.0 . 10^{-4}	$Co^{2+}Ce^{4+}$, Ca^{2+}, V(V)
30	9.0 . 10^{-4}	Cd^{2+}, Zr^{4+}
50	1.5 . 10^{-3}	Tl^+, Mg^{2+}, Mn^{2+}
100	3.0 . 10^{-3}	Citrate, Fe^{3+}, I^-, Hg^{2+}
250	7.5 . 10^{-3}	SCN^-, Ge(IV), $C_2O_4^{2-}$
300	9.0 . 10^{-3}	Tartrate
500	1.5 . 10^{-2}	EDTA, PO_4^{3-}
1 000	3.0 . 10^{-2}	Salicylic acid
5 000	1.5 . 10^{-1}	F^-, SO_3^{2-}, Na^+
>5 000		Br^-, NO_3^-, NO_2^-, SO_4^{2-}, ClO_3^-, ClO_4^-

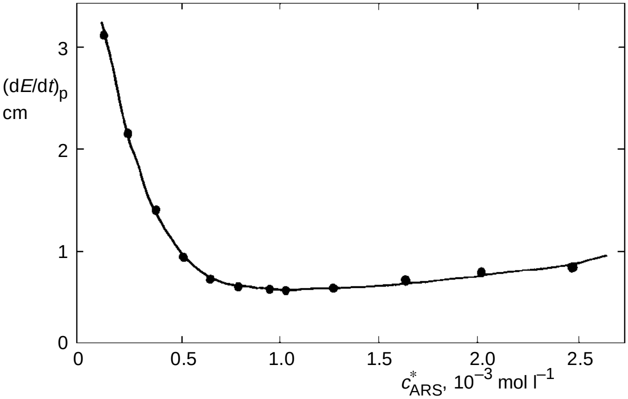


FIG. 5
Influence of concentration of Alizarin S (c^*_{ARS}) for 3.8 . 10^{-5} mol l^{-1} Al^{3+}

TABLE II
Determination of aluminum in real water samples

Samples	Determined $\mu g\ ml^{-1}$	50 ml Water samples[a]			
		Al, μg	added, μg	found, μg	recovery, %
Pure water 1	0.276	13.8	13.7 27.5	28.4 41.2	106 100
Pure water 2	0.568	28.4	13.7	41.2	93
Synthetic water	0.389	19.9	13.7	33.9	102
Boiled water	0.728	18.2	20.6	37.6	94
Tap water	0.149	–	–	–	–
Xuan-Wu		3.17	13.7	17.6	105
lake water	<0.15		27.5	33.1	109
Yang-Zi					
river water	<0.15	–	–	–	–

[a] (1) Synthetic water sample ($Ca^{2+} = Mg^{2+} = 5 \cdot 10^{-5}$ mol l^{-1} and $SO_4^{2-} = NO_3^- = Na^+ = 1 \cdot 10^{-4}$ mol l^{-1});

(2) boiled water sample (taking 25 ml boiled water to 50 ml flask, adding adequate reagents and filled up to the mark with water);

(3) experimental results of other methods,
adsorption CV method: boiled water 0.706 $\mu g\ ml^{-1}$
tap water 0.156 $\mu g\ ml^{-1}$
graphite aas method: tap water 0.15 $\mu g\ ml^{-1}$
Xuan-Wu lake 0.16 $\mu g\ ml^{-1}$
Yang-Zi river 0.19 $\mu g\ ml^{-1}$

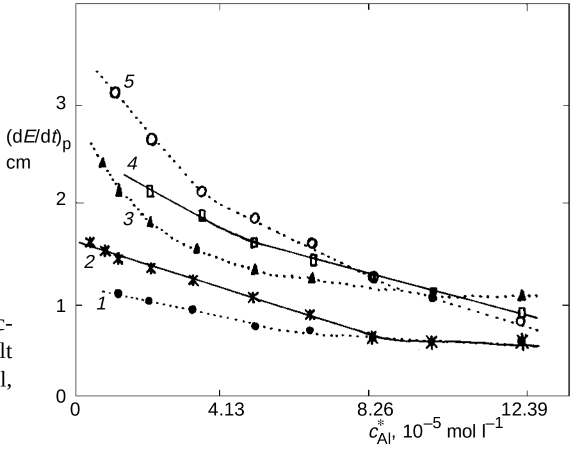


FIG. 6
Influences of different supporting electrolytes (the concentration of each salt is 0.67 mol l^{-1}): (*1*) NH_4Ac, (*2*) KCl, (*3*) $NaNO_3$, (*4*) KNO_3, (*5*) NaCl

Analysis of Aluminum in Real Water Samples

Table II brings the results of determination of Al in pure, synthetic, drinking and natural water (lake and river) samples. It indicates that this method can be satisfactorily used in aluminum analysis of real water samples.

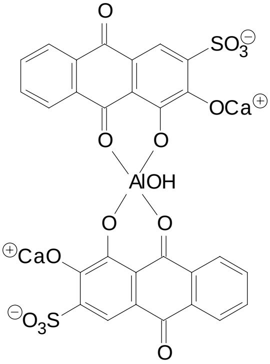


FIG. 7
Complex of Al–Ca-Alizarin

CONCLUSIONS

In this paper, a very simple and fast method for determination of aluminum in natural and drinking waters by ACOP was developed. In practical analysis, many factors must be considered in choosing an appropriate technique for Al. The analyst must consider the availability of instrumentation and the cost of analysis. The specific purpose of this work is to set up a quite simple and inexpensive approach for determining aluminum rather than to improve its analytical sensitivity as many people have done before. Compared with the ordinary adsorptive voltammetry, this method has the distinct advantages of cheap instrumentation, simple and rapid manipulation in which the preconcentration and deaeration are unnecessary. This method is particularly suitable for the fast determination of aluminum in real water samples where the aluminum concentration is about 10^{-6}–10^{-5} mol l^{-1}.

This work is financed by national Natural Science Foundation of China, Fok Ying Tung Education Foundation of Hong Kong and Research Funding of SERC and Analytical Center of Nanjing University. The authors thank Prof. Cheng Rongshi, Chen Hongyuan and Director D. L. Correll of SERC for their support and help. We also thank Dr K. Micka and Prof. R. Kalvoda of J. Heyrovsky Institute of Physical Chemistry and Prof. D. Bustin of Department of Analytical Chemistry, Slovak Technical University for their kindly encouragements. Part of this paper has been presented at the 210th ACS National Meeting, Chicago, on August 20–24, 1995.

REFERENCES

1. Lowe R. D., Snook R. D.: Anal. Chim. Acta *250*, 95 (1991).
2. Cronana C. S., Grigal D. F.: J. Environ. Qual. *24*, 209 (1995).
3. Sposito G. in: *The Environmental Chemistry of Aluminum*, p. 1. CRC Press, Boca Raton 1989.
4. Stara V., Kopanica M.: Collect. Czech. Chem. Commun. *54*, 370 (1989).
5. Tipping E., Backes C. A.: Water Res. *21*, 211 (1987).
6. Ohzhki K., Uno T., Nukatsuka I., Ishida R.: Analyst *113*, 1545 (1988).
7. Heyrovsky J.: Chem. Listy *35*, 155 (1941).
8. Micka K.: Collect. Czech. Chem. Commun. *28*, 1978 (1963).
9. Kalvoda R.: Collect. Czech. Chem. Commun. *34*, 1076 (1969).
10. Micka K.: Collect. Czech. Chem. Commun. *28*, 1957 (1963).
11. Gao H.: Trends Anal. Chem. *1*, 140 (1982).
12. Kalvoda R.: Collect. Czech. Chem. Commun. *22*, 1390 (1957).
13. Kalvoda R.: *Techniques of Oscillographic Polarography*, 2nd ed. Elsevier, Amsterdam 1965.
14. Bi S. P., Du S. D., Gao Hong: J. Electroanal. Chem. *390*, 1 (1995).
15. Bi S. P.: Presented at *207th ACS National Meeting, San Diego, March 13–18, 1994. ANYL 16.*
16. Quint P., Umland F., Sommer H. D.: Z. Anal. Chem. *285*, 359 (1977).
17. Sommer H. D., Umland F.: Z. Anal. Chem. *301*, 203 (1980).
18. Li N. Q., Zhang L., Gao X. X.: Acta Chim. Sin. *50*, 1123 (1992).
19. Li N. Q., Gao X. X.: Chinese J. Anal. Chem. *1*, 40 (1973).
20. Wang L. Z., Chen R. L., Wen S. Q., Zhu J. R.: Chinese J. of Anal. Chem. 15, 118 (1986).
21. Qiuo Z. X.: Acta Chim. Sin. *7*, 86 (1961).
22. Mo M. S.: Li-Hua-Jian-Yan (Chinese) *19*, 35 (1983).
23. Peter G.: Anal. Chem. *55*, 2246 (1983).