

Determination of Aluminum in Drinking Waters by A.C. Oscillopolarography Using Solochrome Violet RS

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A very simple and reliable electroanalytical method for the determination of aluminum in drinking waters by a.c. oscillopolarography using solochrome violet RS is described in this paper. In the buffer solution of 0.1 mol dm^{-3} NaAc— 0.5 mol dm^{-3} KCl (pH 5.2) containing $7 \times 10^{-4} \text{ mol dm}^{-3}$ SVRS, a sensitive incision due to the redox reaction of Al—SVRS complex adsorption wave on the Hg-film electrode was observed on the $dE/dt - E$ oscillogram. The incision depth was linearly proportional to the Al concentration in the range of 5×10^{-7} — $6 \times 10^{-5} \text{ mol dm}^{-3}$ and was used to determine Al quantitatively. The experimental conditions were optimized. No serious interference was found. The detection limit of this method was $2 \times 10^{-7} \text{ mol dm}^{-3}$ and the relative standard deviation was 2.2 % for $5 \times 10^{-5} \text{ mol dm}^{-3}$ Al ($n = 10$). This method was successfully applied to the analysis of Al in real water samples and the results obtained by the proposed method were found to be in good agreement with the results obtained by the ICP-AES method.

The biological significance of aluminum is an important subject [1]. The aluminum salts are often used as flocculating agents in the water treatment factory. In many developing countries, Al was extensively used as utensils for storing drinking waters. It has been reported that there is correlation between the levels of Al in drinking waters and some human diseases including senile dementia, osteomalacia, and gastrointestinal symptoms. Therefore, the determination of Al in drinking waters is critical to evaluate its biological effects. There is currently an increasing interest in the determination of Al by electrochemistry methods [2]. Adsorptive stripping voltammetry is very sensitive with the detection limit of $10^{-9} \text{ mol dm}^{-3}$, but the required procedures of deaeration and preconcentration are vulnerable to contamination and time-consuming [3, 4]. In an attempt to develop a very simple and inexpensive method for determining Al in real water samples with an emphasis on the 10^{-7} — $10^{-5} \text{ mol dm}^{-3}$ range, the use of a.c. oscillopolarography by alizarin S has been examined [5]. However, there are still some problems associated with this method: 1. The sensitivity is not very satisfactory. The detection limit is only $1 \times 10^{-6} \text{ mol dm}^{-3}$, which limits its practical application. 2. High concentrations of Ca(II) or Mg(II) ions interfere with the Al determination. Precipitation with carbonate to remove them from real waters is necessary. This makes the analysis more complicated. In or-

der to overcome these drawbacks, we use solochrome violet RS as the organic complex reagent in the present paper. The application of the a.c. oscillopolarography using this dye to the determination of Al in drinking waters is reported.

EXPERIMENTAL

A laboratory-built experimental setup based on the previous circuit designed by Heyrovský and Kalvoda was utilized to provide the $dE/dt - E$ a.c. oscillogram [6, 7]. A three-electrode system was employed. A mercury film coated on the platinum-based plane electrode (the diameter was 0.5 mm) was used as the working electrode. A platinum foil and a saturated calomel electrode served as the counter and reference electrodes, respectively. The Hg-film electrode was prepared as described by the literature [8]. Prior to use every morning, the electrode had to be conditioned electrochemically at a larger alternating current using the blank solution of 2 mol dm^{-3} NaAc—HAc in the a.c. oscillopolarography mode until a smoothing and steady $dE/dt - E$ charging curve was obtained. The frequency of the alternating current was 50 Hz. The $dE/dt - E$ oscillogram was displayed on an SR-8 oscillograph (Jiangsu Yangzhong Electronic Factory, China). The sensitivity of the oscillopolarograph was $X = 0.5 \text{ V cm}^{-1}$ and $Y = 10 \text{ mV cm}^{-1}$. A 1100 In-

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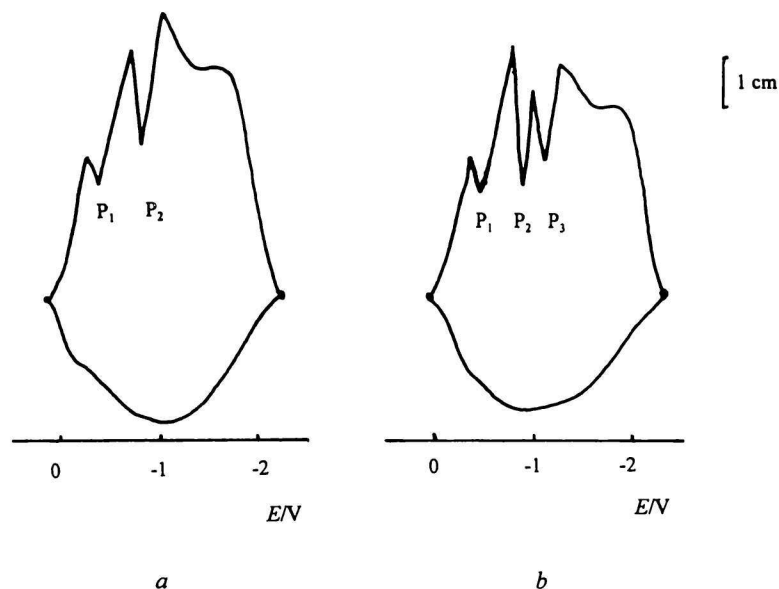


Fig. 1. A.c. oscillograms of SVRS and Al—SVRS complex. a) $0.1 \text{ mol dm}^{-3} \text{ NaAc}$ — $0.5 \text{ mol dm}^{-3} \text{ KCl}$ (pH 5.2) + $7 \times 10^{-4} \text{ mol dm}^{-3} \text{ SVRS}$; b) a with $5 \times 10^{-5} \text{ mol dm}^{-3} \text{ Al}$.

ductively Coupled Plasma (ICP-AES) spectrometer (Jarrell-Ash Company, USA) was used to determine major metal ions concentrations in real water samples. The experiment was carried out at 25°C .

All chemicals used were of anal. grade. The solutions were prepared using twice distilled water from quartz.

A $0.02863 \text{ mol dm}^{-3}$ aluminum stock solution was prepared by dissolving 0.3865 g of high-purity Al powder in 20 cm^3 of $6 \text{ mol dm}^{-3} \text{ HCl}$ and then diluting to 500 cm^3 with water. Working solutions were prepared by appropriate dilution with water.

A 0.01 mol dm^{-3} solochrome violet RS solution was prepared by dissolving adequate amounts of SVRS solid (Aldrich) in 100 cm^3 of water.

A $0.1 \text{ mol dm}^{-3} \text{ NaAc}$ solution was prepared by the dissolution of 82 g of sodium acetate in 1000 cm^3 of water, and the pH was adjusted to 5.2 with $1 \text{ mol dm}^{-3} \text{ HCl}$.

Procedures

A certain amount of Al standard solution was taken in a 80 cm^3 plastic beaker and then 4.5 cm^3 of $0.1 \text{ mol dm}^{-3} \text{ NaAc}$ buffer solution (giving pH 5.2) and 3.5 cm^3 of $0.01 \text{ mol dm}^{-3} \text{ SVRS}$ solution was added. The solution was heated at 90°C for 10 min and cooled at room temperature. After 1 h, 2 g of KCl were added (giving 0.5 mol dm^{-3}) directly to the solution. The solution was transferred into a 50 cm^3 flask and filled to the marked level with buffer solution. Then the solution was transferred into the electrolytic cell. The electrode system was immersed in the solution and the constant-current circuit was connected letting the alternating current pass through

the Hg-film and counter electrodes. The solution was stirred with a magnetic bar. After adjusting suitable electronic parameters and waiting for 3 min, the incision depth was recorded as the function of the Al concentrations.

RESULTS AND DISCUSSION

A.C. Oscillograms of Solochrome Violet RS and its Complex with Al

The a.c. oscillograms of the SVRS and its complex with Al are shown in Fig. 1. In the buffer solution containing only SVRS, two sharp incisions P_1 and P_2 appeared at the potentials of -0.40 and -0.80 V , respectively. They are due to the adsorption reactions of SVRS on the surface of Hg electrode. In the presence of $5 \times 10^{-5} \text{ mol dm}^{-3} \text{ Al}$, a sharp incision P_3 , reflecting the adsorption reaction of the Al—SVRS complex, occurred at the potential of -1.00 V on the oscillogram. The mechanisms of the electrode reactions are the same as those described by Wang [9], Perkins and Reynolds [10], and Florence and Belew [11]. For this reason, all mechanistic discussions were omitted. The incision depth (h) increased as a linear function with increasing Al concentrations and could be used to determine Al in solution.

Optimization of Variables

Various experimental variables affecting the a.c. oscillographic response of the Al—SVRS complex were evaluated and optimized.

The dissolved oxygen in solution did not interfere with the electrode reaction of the Al—SVRS complex.

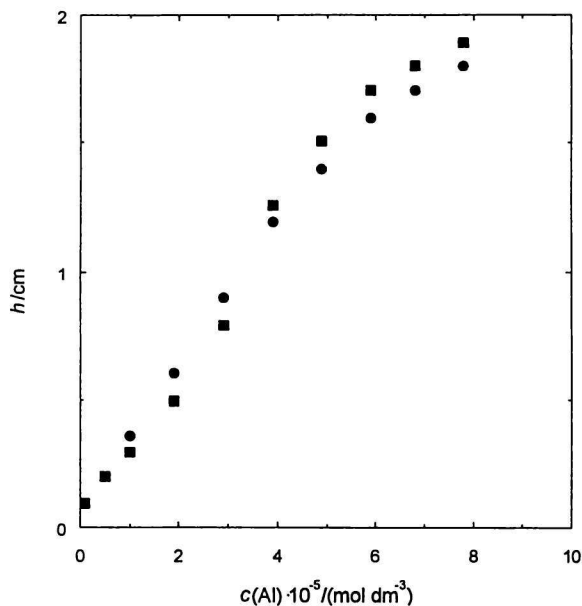


Fig. 2. Working curves for the determination of Al in the presence of dissolved oxygen (●) and after deaeration (■). Other conditions as in Fig. 1.

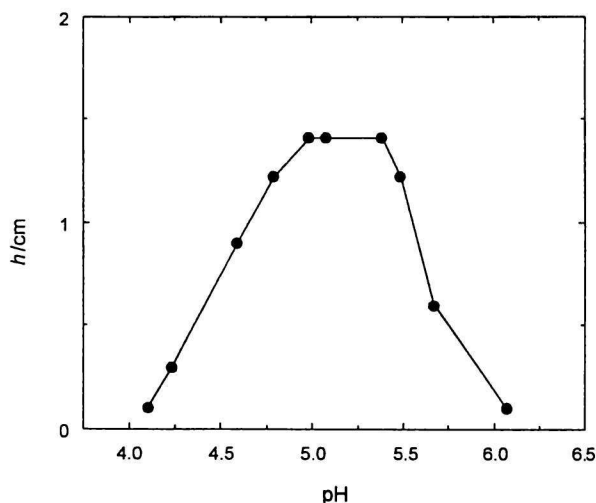


Fig. 3. Influence of pH on the incision depth. Other conditions as in Fig. 1.

The calibration graphs for both cases are almost the same (Fig. 2). Thus, the deaeration procedure was omitted and the determination was performed in air-saturated solution.

The effect of the solution pH on the incision depth for the Al—SVRS complex was studied over the range of 4–6. It was found that the incision depth was constant at pH values between 5.0 and 5.4, whereas the incision rapidly diminished and disappeared at pH < 5.0 or pH > 5.4 (Fig. 3). Therefore, pH 5.2 was chosen as the optimal pH value.

The influence of the concentration of solochrome

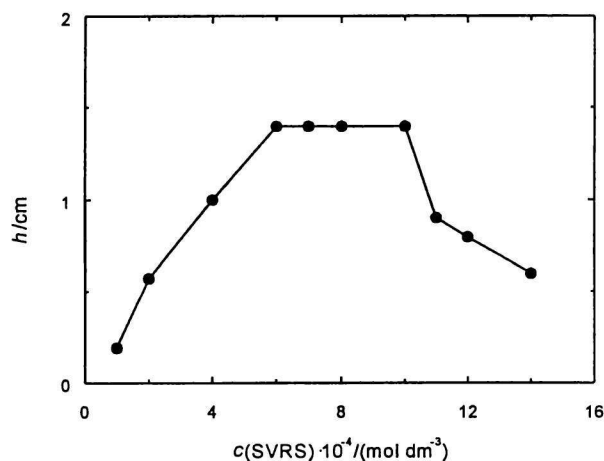


Fig. 4. Influence of SVRS concentration on the incision depth. Other conditions as in Fig. 1.

violet RS on the incision depth was examined. Fig. 4 indicates that the incision depth increased strongly with the SVRS concentration up to about $6 \times 10^{-4} \text{ mol dm}^{-3}$, then remained constant up to a concentration $1 \times 10^{-3} \text{ mol dm}^{-3}$ before decreasing at the SVRS concentrations higher than $1 \times 10^{-3} \text{ mol dm}^{-3}$. Thus, a SVRS concentration of $7 \times 10^{-4} \text{ mol dm}^{-3}$ was recommended.

Several different salts were tested for the suitability to produce a perfect $dE/dt - E$ oscillogram as the supporting electrolytes. Experimental results indicate that the use of KCl can achieve the best result, whereas other salts (KNO_3 , NaNO_3 , NaCl , and NH_4Ac) were not chosen. The influence of the KCl concentration was also inspected and the optimal value was 0.5 mol dm^{-3} (Fig. 5).

Forced convection during the determination of Al affected the resulting a.c. oscillographic response by increasing the rate of transport of Al—SVRS molecules to the surface. A 5-fold incision depth enhancement was obtained for a stirred ($\approx 500 \text{ min}^{-1}$) solution compared to a quiescent one. Therefore, the solution was stirred with magnetic bar under a moderate stirring speed of 500 min^{-1} throughout the experiment.

The Stability, Repeatability, Detection Limit, and Linear Working Range

The stability and repeatability of this method for determining Al are excellent. For $5 \times 10^{-5} \text{ mol dm}^{-3}$ Al, the incision depth is $(1.4 \pm 0.1) \text{ cm}$ in the period of 50 min and the relative standard deviation is 2.2% ($n = 10$). The detection limit of this method is $2 \times 10^{-7} \text{ mol dm}^{-3}$ (defined as the minimum concentration of Al yielding the shallowest incision on the $dE/dt - E$ oscillogram at the potential of -1.00 V) and the linear working range is 5×10^{-7} to $6 \times 10^{-5} \text{ mol dm}^{-3}$.

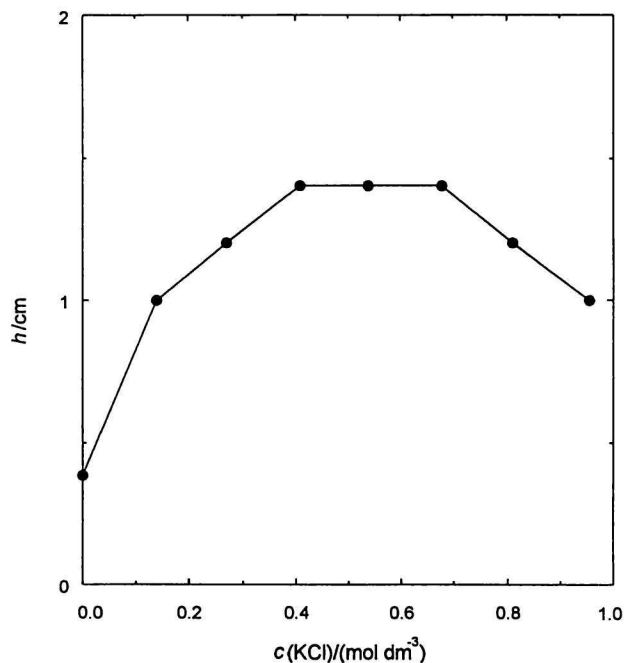


Fig. 5. Influence of KCl concentration on the incision depth. Other conditions as in Fig. 1.

Analysis of Aluminum in Real Water Samples

A number of foreign ions were examined for interference in the assay. For the determination of 5×10^{-5} mol dm⁻³ Al, the results have shown that a 1000-fold excess of Sr(II), Si(IV), SO₄²⁻ or SO₃²⁻, 300-fold excess of Ca(II), EDTA or NO₃⁻, 150-fold excess of Mg(II) or F⁻, 80-fold excess of SCN⁻, citrate, Hg(II), salicylic acid, tartrate, C₂O₄²⁻ or phosphate, 50-fold excess of Ge(IV), NO₂⁻ or La(III) do not interfere. Also a 30-fold excess of Ba(II) or Tl(I), 10-fold excess of Bi(III), Cd(II), Pb(II), Ce(IV) or Mn(II) and 1-fold excess of Ni(I), Co(II), Cu(II), Fe(III), In(III), Zn(II), Sn(II) or Ga(III) do not interfere. Because the amounts of ma-

ior interfering species present in drinking waters are very low compared with that of Al [12], they will not cause any interference for determining Al. The interfering of Fe and Cu ions can be effectively eliminated by adding of 0.1 % DDTC and 0.1 % N(CH₂COOH)₃, respectively. The real water samples were prepared as follows: The tap water was drawn from the local water supply while the mineral waters were obtained from the supermarket. Boiled waters were prepared by boiling the distilled water in aluminum pot for different times. The general procedure for determining Al in real water samples was: an adequate volume of water sample solution was pipetted into the 80 cm³ beaker, then 4.5 cm³ of 0.1 mol dm⁻³ NaAc buffer solution was added (giving pH 5.2), followed by 3.5 cm³ of 0.01 mol dm⁻³ SVRS solution. The subsequent steps were as in the basic procedure. The standard addition method was used for calibration purposes. Table 1 gives the results for determining Al in real drinking water samples. There is a good accordance between the results obtained by this method and those obtained by ICP-AES. (The water quality data of the samples are listed in Table 2. No obvious interference was found.)

CONCLUSION

In conclusion, the present study describes an effective means for the determination of the trace levels of Al in drinking waters. It provides an efficient and versatile alternative approach to ICP-AES. Besides the merits of a.c. oscillography mentioned before (cheap instrumentation, simple manipulation, and no removing oxygen needed), the proposed technique using SVRS still possesses some distinct advantages compared with that by DASA: 1. Improved resolution. The resolution of Al—SVRS with SVRS (P₂, P₃) is 0.2 V, better than that of Al—DASA with DASA (0.11 V). 2. Enhanced sensitivity and extended linear working range (while using DASA the linear range is from

Table 1. Determination of Aluminum in Drinking Water Samples (mol dm⁻³)

Sample	Determined by this method	Added	Found	Recovery %	ICP-AES method
1 Synthetic water 1	6.7×10^{-6}	7.2×10^{-6}	13.8×10^{-6}	99	6.7×10^{-6}
2 Synthetic water 2	1.8×10^{-6}	1.8×10^{-6}	3.6×10^{-6}	100	1.7×10^{-6}
3 10-min boiled distilled water	2.5×10^{-6}	1.8×10^{-6}	4.2×10^{-6}	96	2.6×10^{-6}
4 20-min boiled distilled water	5.6×10^{-6}	3.6×10^{-6}	9.2×10^{-6}	100	5.6×10^{-6}
5 Tap water	5.5×10^{-6}	5.4×10^{-6}	10.8×10^{-6}	98	5.6×10^{-6}
6 Chengde mineral water B	4.5×10^{-6}	5.4×10^{-6}	10.0×10^{-6}	102	4.4×10^{-6}
7 Chengde mineral water C	6.7×10^{-6}	7.2×10^{-6}	13.8×10^{-6}	99	6.7×10^{-6}
8 Wa-Ha-Ha mineral water	4.4×10^{-6}	5.4×10^{-6}	9.8×10^{-6}	100	4.4×10^{-6}
9 Le-Bai-Shi mineral water	$< 2.0 \times 10^{-7}$	—	—	—	$< 3.7 \times 10^{-7}$ (10 ppb)
10 Geyser distilled water	$< 2.0 \times 10^{-7}$	—	—	—	$< 3.7 \times 10^{-7}$ (10 ppb)

Table 2. Water Quality Data of the Drinking Waters (mg dm⁻³)*

Sample	3	4	6	7	8	9	10
K(I)	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	2.1	< 0.3
Na(I)	0.32	0.25	10.1	18.4	10.2	4.1	0.5
Ca(II)	2.0	3.0	71.5	123	58.8	2.3	0.63
Mg(II)	1.1	1.9	6.4	15.1	2.8	0.47	0.07
Ba(II)	0.02	0.018	0.02	0.07	0.008	0.011	0.001
Sr(II)	0.017	0.026	0.19	0.48	0.23	0.01	0.003
Si(IV)	2.4	4.4	8.4	12.4	20.3	15.4	0.05
Mn(II)	0.10	0.01	0.003	0.004	0.002	0.001	0.002
Zn(II)	0.08	0.05	0.15	0.04	< 0.002	< 0.002	< 0.002
Cl ⁻	2.9	4.1	5.7	52.3	2.5	0.7	-
SO ₄ ²⁻	2.8	4.2	4.1	14.6	3.3	-	-
NO ₃ ⁻	-	-	22.2	96.2	5.0	-	-

*By ICP-AES and ion chromatography.

For all waters (mg dm⁻³): Fe(II) + Fe(III) < 0.015, Cu(II) < 0.002, Cd(II) < 0.002, Pb(II) < 0.025, Li(I) < 0.006, Ni(II) < 0.01, Co(II) < 0.003, Mo(II) < 0.005, V(V) < 0.002, Cr(VI) < 0.005.

5×10^{-6} to 5×10^{-5} mol dm⁻³). 3. Minimized interference of Ca(II) or Mg(II), which are the abundant cations in the drinking waters. On the other hand, the film-mercury electrode is much simpler to handle than the HMDE, particularly in the flow-analysis mode. It makes the application of this technique to the flow injection analysis mode and automation possible. Ongoing research work is now being carried out in our laboratory.

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