

## VOLTAMMETRIC DETERMINATION OF TRACE AMOUNTS OF ALUMINIUM

Věra STARÁ and Miloslav KOPANICA

*UNESCO Laboratory of Environmental Electrochemistry at the  
J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, 182 23 Prague 8*

Received March 21, 1988

Accepted May 3, 1988

---

Aluminium is determined voltammetrically in the form of the aluminium complex with Acid Alizarin Violet N in an acetate buffer of pH 5.2 using a hanging mercury drop electrode and the d.c. or differential pulse technique. A linear dependence between the peak current and the aluminium concentration was obtained in the range from  $2 \cdot 10^{-8}$  to  $5 \cdot 10^{-6}$  mol l<sup>-1</sup>. The interfering effect of copper, lead and cadmium is eliminated by the auxiliary complex forming reagent — glycine.

---

The determination of trace amounts of aluminium is usually carried out using optical methods of analysis. Electrochemical methods are seldom applied in these determinations. The indirect polarographic determination of aluminium is based on the electrochemical reduction of the complex formed between some di-*o*-hydroxyazo dyes and aluminium as reported by Willard and Dean<sup>1</sup>. The polarographic behaviour of these complexes and their analytical application was thoroughly studied by Florence et al.<sup>2-4</sup>. The limit of detection for the polarographic determination of aluminium was reported to be 1 ppm (ref.<sup>5</sup>). Recently, Wang et al.<sup>6</sup> reported a voltammetric method for the determination of aluminium based on the adsorptive accumulation of the aluminium complex with Solochrom Violet on the surface of a hanging mercury drop electrode.

This work shows that aluminium complex with Acid Alizarin Violet N can be used for a highly sensitive voltammetric determination.

### EXPERIMENTAL

#### Equipment and Method

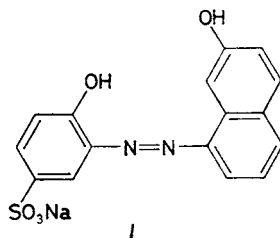
The microcomputer controlled electrochemical analyzer ECM-700 (ZWG, Berlin, G.D.R.) was used for all the measurements. The static mercury drop electrode EST of the same manufacturer was used as the working electrode. A saturated calomel reference electrode (SCE) and platinum wire counter electrode were used.

The potential-scan rate was  $2 \text{ mV s}^{-1}$  in d.c. polarographic measurement and  $20 \text{ mV s}^{-1}$  in d.c. voltammetry; in differential pulse voltammetry the pulse length was 80 ms and the interval between the pulses 200 ms.

The analyzed solutions were degassed with argon.

### Reagents

The sodium salt of Acid Alizarin Violet N(I) (C.I.15670), the product of Aldrich Chem. Corp. Inc. (U.S.A.) was purified by two crystallizations from ethyl alcohol. A  $10^{-3} \text{ mol l}^{-1}$  solution of Acid Alizarin Violet N(I) was prepared by dissolving the reagent in water.



The acetate buffer solution was prepared by adding 1%  $\text{HClO}_4$  to a 0.1M sodium acetate solution to attain a pH value of 5.3.

All the other solutions were prepared from p.a. chemicals. Twice distilled water (a quartz apparatus) was used throughout.

### Procedure

A 2.5 ml acidic sample solution containing from 0.005 to 0.5  $\mu\text{g}$  Al per ml is transferred to a 25 ml volumetric flask and 5 ml of 0.1M glycine solution are added. This mixture is diluted to approx. 20 ml with the 0.1M acetate buffer solution (pH 5.3) and 0.1 ml of 0.6% reagent I is added. The resulting solution is heated on a water bath to approx.  $80^\circ\text{C}$  for 15 min. After 1 hour, the flask is filled to the mark with the buffer solution. A d.c. or d.p. voltammetric curve of this solution is recorded in the potential range from  $-0.15$  to  $-0.70 \text{ V}$  (SCE). The height of the peak with the peak potential value,  $-0.45 \text{ V}$ , corresponding to the reduction of Al-I complex is measured and the content of aluminium is evaluated using a calibration plot.

If the aluminium content is very low, the peak of the reagent ( $E_p = 0.30 \text{ V}$ ) is too high and the peak of the aluminium complex cannot be measured precisely. The determination is then repeated using the given procedure and only 0.02 ml of the reagent I are added.

## RESULTS AND DISCUSSION

### *Polarographic Behaviour of Aluminium-I Complex*

In slightly acidic media the reagent I yielded a d.c. polarographic wave with a half-wave potential ( $E_{1/2}$ ) of  $-0.30 \text{ V}$  (SCE) (pH 5.3) corresponding to the reduction of the  $-\text{N}=\text{N}-$  group. When the solution contained aluminium(III) ions and a ten times molar excess of the reagent (the mixture of the reagent and aluminium(III)

ions was prepared separately and used 10 hours after mixing, because of slow formation of the complex) another wave was observed at more negative potential, the half-wave potential of this wave depended on the pH value of the supporting electrolyte. The limiting current of the more negative wave increased with enhancing aluminium complex concentration and increased linearly with raising mercury reservoir height.

The cyclic voltammogram of the aluminium-*I* complex recorded in the acetate buffer medium of pH 5.3 yielded two cathodic peaks ( $E_p$  values  $-0.35$  and  $-0.55$  V (SCE)) and no anodic peak. When the polarization cycles were repeated with an identical drop electrode, the height of the cathodic peaks decreased. When the working electrode was kept at the potential  $-0.10$  V for 30 s before the cyclic polarization was started, the heights of both peaks increased.

The cyclic voltammograms recorded at various potential scan rates showed that the heights of both the cathodic peaks increased with increasing potential scan rate in the range from 20 to 1 000  $\text{mV s}^{-1}$ . On the basis of these results it was supposed that the reagent and the aluminium complex are adsorbed on the surface of the mercury electrode and the adsorbed species are irreversibly reduced.

#### *Voltammetric Determination of Aluminium*

Similar to other azo dyes, the reaction between aluminium(III) and *I* proceeds slowly. The mixture of the reagent and aluminium(III) ions was therefore mixed at an appropriate pH value, heated to approx.  $80^\circ\text{C}$  for 15 min on a water bath and the corresponding voltammograms were recorded after different time intervals. The peak height for the aluminium complex attained the maximum value 90 min after mixing. The optimum pH value for the complex formation was determined from the experiments, in which the reagent and aluminium(III) ions were mixed at different pH values and the voltammograms were recorded two hours after mixing. The corresponding peak current ( $i_p$ ) and peak potential ( $E_p$ ) values are summarized in Table I.

The data in Table I show also the effect of the accumulation of the aluminium complex. The extent of accumulation was almost unaffected by variation of the accumulation potential in the range from  $+0.10$  to  $-0.20$  V (SCE). The peak current increased with increasing accumulation time only over a short interval (60 s at the aluminium concentration level  $10^{-6}$   $\text{mol l}^{-1}$  and 120 s at  $10^{-8}$   $\text{mol l}^{-1}$  concentration level), when the solution was not stirred. Stirring during the accumulation period resulted in distorted peaks.

The measurements on solutions with various aluminium concentrations prepared according to the given procedure yielded linear dependence between the peak current values (measured at  $-0.49$  V (SCE)) and the aluminium concentration in the region from  $2 \cdot 10^{-8}$  to  $5 \cdot 10^{-6}$   $\text{mol l}^{-1}$ . For lower aluminium concentrations ( $10^{-8}$  to  $10^{-7}$   $\text{mol l}^{-1}$ ), the differential pulse mode was applied and d.c. voltammetry was

used for high aluminium concentration levels. The data for the corresponding regression straight lines are for the concentration range  $2 \cdot 10^{-8}$  to  $5 \cdot 10^{-7}$  mol l<sup>-1</sup>: slope 0.04 nA l nmol<sup>-1</sup>, intercept 11.68 nA, standard deviations  $s_{yx}$  0.43 and correlation coefficient 0.9987; for the concentration range  $5 \cdot 10^{-7}$  to  $5 \cdot 10^{-6}$  mol l<sup>-1</sup>: slope 0.04 nA l nmol<sup>-1</sup>, intercept -0.77 nA, standard deviation  $s_{yx}$  1.29 and correlation coefficient 0.9998.

Interfering effects caused by the presence of copper(II), lead(II) and cadmium(II) ions were eliminated by an auxiliary complex forming reagent. Glycine was found as the most suitable reagent for this purpose because it forms with interfering metal ions (Cu<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>) more stable complexes than the reagent *I* and further glycine does not compete with the formation of the aluminium-*I* complex. Ligands forming more stable complexes with aluminium(III) ions, as e.g. ethylenediamine-tetraacetic acid or nitrilotriacetic acid, prevent the formation of the aluminium-*I* complex and thus make the determination impossible. A relatively high amount of glycine was used for masking, a total glycine concentration of 0.01 mol l<sup>-1</sup> was used for the determination of aluminium in the concentration range  $10^{-5}$  to  $5 \cdot 10^{-6}$  mol l<sup>-1</sup> and 0.005 mol l<sup>-1</sup> glycine solution for the concentration range  $10^{-8}$ – $10^{-7}$  mol l<sup>-1</sup>. The sensitivity of the proposed method is nearly identical with the method of adsorptive voltammetry of aluminium based on the accumulation of aluminium-Solochrome Violet complex.

The described method was tested by the determination of aluminium in used motor-oils. The metals were separated from the oil by extraction with nitric and hydrochloric acid. The extract was diluted with water, neutralized with potassium hydroxide and aluminium was determined in the resulting solution by the described procedure. Three oil samples containing according to the spectrophotometric deter-

TABLE I

Peak current and peak potential values of aluminium-*I* complex at different pH values. Accumulation at -0.10 V in unstirred solution, measured two hours after mixing, Al<sup>3+</sup> concentration  $10^{-7}$  mol l<sup>-1</sup>, *I* concentration  $10^{-6}$  mol l<sup>-1</sup>, DPV, HMDE

pH	$i_p$ , nA		$E_p$ , V
	$t_{acc} = 0$ s	$t_{acc} = 60$ s	
3.0	2.5	10.0	-0.38
4.0	85.0	155.0	-0.42
4.7	130.0	210.0	-0.47
5.0	260.0	560.0	-0.49
5.3	305.0	630.0	-0.49

mination using 8-hydroxyquinoline 53.0, 35.0 and 21.0  $\mu\text{g ml}^{-1}$  Al, were analyzed by the described method and the corresponding results were found to be  $52.0 \pm 0.6$ ,  $34.0 \pm 0.5$  and  $20.0 \pm 0.8 \mu\text{g ml}^{-1}$  Al.

#### REFERENCES

1. Willard H. H., Dean J. A.: *Anal. Chem.* 22, 1264 (1950).
2. Florence T. M., Smythe L. E.: *Nature* 187, 771 (1960).
3. Florence T. M., Izarp D. B.: *Anal. Chim. Acta* 25, 386 (1961).
4. Florence T. M., Aylward G. H.: *Aust. J. Chem.* 15, 65 (1962).
5. Florence T. M.: *Anal. Chem.* 34, 496 (1962).
6. Wang J., Farias P. A. M., Mahmoud J. S.: *Anal. Chim. Acta* 172, 57 (1985).

Translated by the author (M.K.).