

## Alizarin Red S modified electrochemical sensors for the detection of aluminum ion

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Abstract

Alizarin Red S modified screen printed carbon electrodes were developed for the electrochemical detection of aluminum ion. The electrodes developed use screen-printed carbon electrodes (SPCEs) coupled with chemical modification with an organic chelator, Alizarin Red S (ARS), for aluminum ion detection in aqueous solution. For sensor fabrication ARS was directly immobilized on the surface of SPCEs using PVA-SbQ (The poly(vinyl alcohol) bearing stryrylpyridinium groups). Aluminum concentrations were indirectly estimated by amperometric determination of the non-complexed ARS immobilized on the electrodes, after its complexation with aluminum. The sensitivity of the sensor developed was  $3.8 \text{ nA}\mu\text{M}^{-1}\text{cm}^{-2}$  and the detection limit for aluminum was  $25 \mu\text{M}$ .

**Key Words** : screen printed electrode, electrochemical, alizarin red S, aluminum ion

### 1. Introduction

Direct determination of aluminum (Al(III)) ions by voltammetric and amperometric methods using solid electrodes is limited for application to real samples because of a low signal-to-noise ratio<sup>[1]</sup> and high reduction potential of Al(III)<sup>[2]</sup>. These limitations could be overcome by using indirect methods based on the electrodes modified with metal chelators such as Alizarin Red S<sup>[3-6]</sup>. These methods are based upon the measurement of changes in the electrochemical behavior of the chelator upon complexation with the Al(III).

Chemically modified electrodes (CMEs)<sup>[10]</sup> have been widely used for the electrochemical determination of metals in water resources<sup>[7]</sup>. CMEs, generally, have been used in voltammetric methods especially in anodic stripping voltammetry (ASV) with an analyte accumulation step. The modifiers, chelators, are physically or chemically modified onto the working electrode and used to accumulate the analyte followed by the indirect determination of the analyte. The reagents used for chemical modification of the electrode surface therefore fall into two main categories; accumulating reagents

and electro-active reagents. The use of CMEs in electrochemical analysis has led to the development of sensors exhibiting high selectivity and sensitivity for Al(III) ion in environmental water samples.

The work reported in this study is aimed at developing a rapid, sensitive and specific technique for the measurement of Al(III). The technique involved the use of an organic chelator, Alizarin Red S (ARS), modified disposable screen-printed carbon electrodes for the electrochemical determination of Al(III) ion in aqueous samples.

To achieve the aim proposed, this study was focused in two major areas. Firstly, the differences in electrochemical behavior between modified ARS and its complexed form with Al(III) was characterized and optimized using voltammetric and amperometric techniques. Secondly, disposable printed electrodes modified with immobilized ARS using the photo-polymer, PVA-SbQ<sup>[8,9]</sup>, for amperometric Al(III) detection was fabricated and tested.

### 2. Experimental

#### 2.1. Materials

The basic disposable screen-printed carbon electrodes (SPCEs) were constructed as reported by author previously<sup>[8]</sup>. Alizarin Red S (ARS, 3,4-dihydroxy-9,10-

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dioxo-2-anthracensulfonic acid, sodium salt), aluminum nitrate( $\text{Al}(\text{NO}_3)_3$ ), potassium chloride(KCl), and potassium phosphates( $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ ) were obtained from Sigma. The poly(vinyl alcohol) bearing stryrylpyridinium groups(PVA-SbQ) matrix(SPP-H-13) was from Toyo Gosei Kogyo Co.(Tokyo, Japan).

## 2.2. Apparatus

Cyclic voltammetry and amperometric measurements were performed using an Autolab analyzer supplied by Eco Chemie B.V.(Utrecht, Netherlands). A Perspex 10-well template for accommodation of the screen-printed electrodes was built by the Workshop at Pusan National University. A Spectroline<sup>®</sup> UV lamp was obtained from Spectronics Co.(New York, USA) and was used for PVA-SbQ photo-polymerisation. pH measurement was performed using an Orion pH meter model 310 in conjunction with a PerpHecT<sup>®</sup> Ag/AgCl pH electrode model 9202 supplied by Orion<sup>®</sup> Research Inc.(Beverly, USA).

## 2.3. Alizarin Red S(ARS) Solution

55 mM Alizarin Red S(ARS) solution was prepared by dissolving 20 mg of ARS in 20 ml of 50 mM potassium phosphate buffer(PPB, pH 7.0, 100 mM KCl). 2 ml aliquots of ARS solutions were also prepared in the same buffer, over the concentration range of 0.5 mM~55 mM.

## 2.4. Assessment of ARS Modified SPCEs(PVA-SbQ(ARS)-SPCEs)

ARS was modified in the photo-polymer(PVA-SbQ) layer on the surface of the working electrodes. A 200  $\mu\text{l}$  aliquot of 55 mM ARS solution was thoroughly mixed with 300  $\mu\text{l}$  of PVA-SbQ prepolymer for 5 minutes. A 5  $\mu\text{l}$  aliquot of the mixture was placed on the surface of the working electrode of the SPCEs. The electrodes were then exposed to long wave UV light(365 nm, at 10 cm) for 2 h to allow polymerization, and dried in a dark place for 12 h at room temperature. 40  $\mu\text{mol}$  of ARS was modified on each SPCE. In order to investigate the voltammetric behavior of ARS in PPB, PVA-SbQ(ARS)-SPCEs were also prepared using the 2 ml aliquots of ARS solutions as described in Section 2.3.

## 2.5. Measurement Procedure

An electrochemical cell for voltammetric and amper-

ometric measurements was set up and Cyclic voltammetry was carried out using polymer coated bare SPCEs and PVA-SbQ(ARS)-SPCEs and were used according to the procedure outlined in previous studies by author<sup>[8,9]</sup>. Experimental protocols were identical except for the following conditions; 50 mM PPB was used as background electrolyte and the potential sweeping range was between -0.1 mV to +1.0 mV vs. Ag/AgCl at a scan rate of 50  $\text{mVs}^{-1}$ . Amperometric measurements were performed using PVA-SbQ(ARS)-SPCEs as described in previous studies by author<sup>[8,9]</sup>. Electrodes were polarized at a potential of +480 mV vs. Ag/AgCl in PPB. This was repeated to construct aluminum calibration curves for a range of Al(III) concentrations from 0 to 5 mM using a fresh PVA-SbQ(ARS)-SPCE for each measurement.

## 3. Results and Discussion

### 3.1. Cyclic Voltammetry of Alizarin Red S

Cyclic voltammograms with bare(PVA-SbQ-SPCEs) and ARS modified electrodes(PVA-SbQ(ARS)-SPCEs) were obtained in 50 mM PPB(pH6.0, 100 mM KCl) and a representative example is shown in Fig. 1. Potential sweeping was initiated in an anodic direction from -0.1 V in all experiments.

As can be seen in curve B in Fig. 1, no specific oxi-

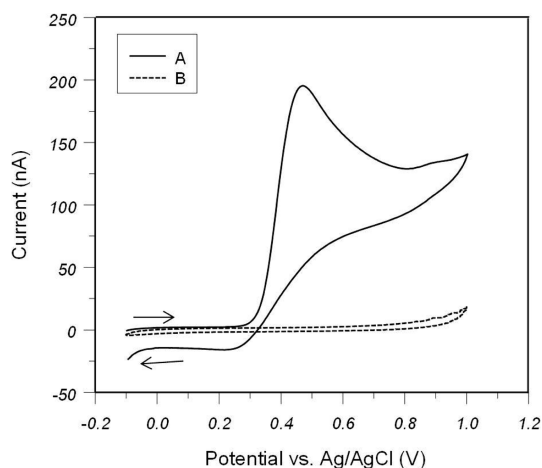


Fig. 1. Cyclic voltammograms for PVA-SbQ(ARS)-SPCEs (A) and PVA-SbQ-SPCEs (B) in 50 mM PPB (pH6.0, 100 mM KCl).

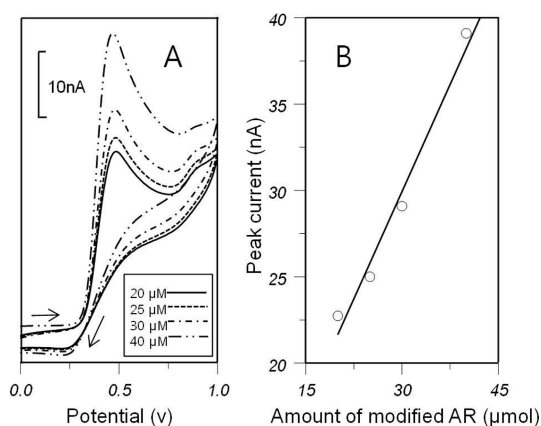


Fig. 2. A: Cyclic voltammograms for PVA-SbQ(ARS)-SPCEs in 50 mM PPB (pH 6.0, 100 mM KCl). Experimental conditions; Scan range was from -0.1 V to +1.0 V at a scan rate of  $50 \text{ mVs}^{-1}$  and scan started at -0.1 V. Amounts of modified ARS at each electrode were 20, 25, 30 and 40  $\mu\text{mol}$ . B: Plot of peak current vs. amount of modified ARS from voltammograms in A.

dation and reduction current peaks were observed in the absence of modified ARS over the total sweep range of -0.1 V to +1.0 V. In the case of cyclic voltammograms for PVA-SbQ(ARS)-SPCEs, a clear anodic peak was apparent at a potential of +0.48 V with an anodic peak current of 190 nA and is shown in curve A in Fig. 1. After sweeping 5 times at potentials between -0.1 and +1.0 V, the peak current remained practically constant, which indicated the strong and stable modification of ARS on the surface of the electrodes.

Fig. 2 shows examples of cyclic voltammograms for PVA-SbQ(ARS)-SPCEs that were modified with a series of ARS concentrations. The final amounts of ARS modified at each electrode ranged from 20 to 40  $\mu\text{mol}$ . As can be seen, the peak heights produced were proportional to the amount of ARS on the modified surface.

The voltammetric behavior of ARS is known to be quasi-reversible, showing redox peaks at potentials over the range -0.6 to -0.8 V vs. SCE when graphite working electrodes were used<sup>[2]</sup>. In this range of potentials, however, the voltammograms obtained using the electrodes under investigation in this study showed a large cathodic peak and high noise. Although ARS could produce redox peaks at negative potentials, the electro-

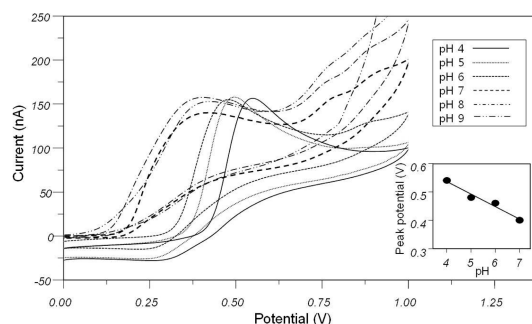


Fig. 3. Cyclic voltammograms for PVA-SbQ(ARS)-SPCEs in 50 mM PPB (pH 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0, 100 mM KCl). Inset: linear relationship between peak potential and pH.

chemical behavior would be subject to interference from the reduction of dissolved oxygen<sup>[11]</sup>. This would lead to major irreproducibility problems. As a result of these considerations, therefore, the potential range from -0.1 to +1.0 V was used for all cyclic voltammetric experiments.

The cyclic voltammograms for PVA-SbQ(ARS)-SPCEs were sensitively dependent on the change of pH. As can be seen in Fig. 3, peak potentials shifted as a function of pH. At higher pH over 6, however, the quasi-reversible behavior of ARS was deformed compared with the voltammograms obtained at lower pH. At pH 7 to 9, the large cathodic picks were produced at potentials higher than 800 mV vs. Ag/AgCl and the peaks were broadened. It was, consequently, difficult to determine reproducible peak potentials. Therefore, pH 6 was used as an operating pH for further voltammetric experiments. The inset in Fig. 3 shows a linear relationship between the peak potentials and pH from 4 to 7. The slope for the line was calculated to be;  $\Delta E_p / \Delta \text{pH} = -44 \text{ mV/pH}$ .

### 3.2. Voltammetric Detection of Al(III)

In the presence of Al(III), the change in cyclic voltammograms of PVA-SbQ(ARS)-SPCEs is shown in Fig. 4. As can be seen, the peak potentials are nearly constant while the magnitude of anodic peak current is decreased as a function of the increase in aluminum concentration in solution. The responses of ARS modified electrodes showed a similar peak current decrease with a series of Al(III) samples measured over the pH range from 5 to 8. In recent studies, however, it was

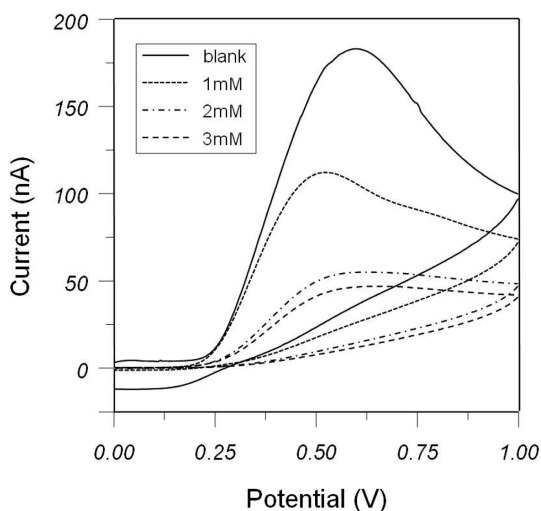


Fig. 4. Cyclic voltammograms for PVA-SbQ(ARS)-SPCEs in 50 mM PPB (pH 6.0, 100 mM KCl) with blank, 1.0, 2.0, and 3.0 mM Al(III).

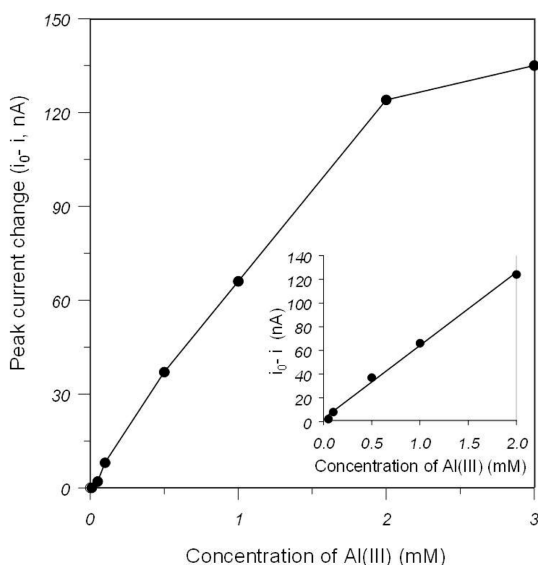


Fig. 5. Calibration curve of anodic peak currents from voltammograms obtained using PVA-SbQ(ARS)-SPCEs vs. Al(III) concentration in 50 mM PPB (pH 6.0, 100 mM KCl). Inset: linear relationship between peak current and Al(III) concentration over the range of 0.05-2.0 mM.

demonstrated that ARS modified electrodes could be used for the detection of copper in water at pH 8.0-9.0<sup>[3,4]</sup>. Furthermore, at pH 6.0, it was apparent that the

anodic peak from the voltammogram had a much smaller peak width compared with the peak at pH 7.0. Therefore, pH 6.0 was chosen as the operating pH in all further experiments

In order to obtain data for calibration curves for Al(III), cyclic voltammograms were obtained with Al(III) concentrations over the range from 0 to 3 mM. Peak currents were determined from the first scan of each voltammogram. Calibration curves for Al(III) were constructed using the data from the cyclic voltammograms obtained and are shown in Fig. 5. The peak current change ( $i_p - i$ ) in Fig. 5, represents the differences between peak currents determined by using Al(III) samples and the peak current obtained from the blank. Although the calibration curve showed a wide range of linearity, approximately from 0.05 mM to 2.0 mM Al(III) and the sensitivity of the electrodes for Al(III) was determined to be  $0.63 \mu\text{A mM}^{-2}$ .

### 3.3. Amperometric Detection of Al(III)

Amperometric measurements were performed with Alizarin Red S modified screen-printed carbon electrodes (PVA-SbQ(ARS)-SPCEs) as described. Steady baseline currents were observed after 5 minutes ~10 minutes when the PVA-SbQ(ARS)-SPCEs were polarized at a potential of +480 mV. The steady state current observed was produced by oxidation of ARS, which was modified in the polymer layer on the surface of the electrodes. After addition of a 10  $\mu\text{l}$  aliquot of an Al(III) sample into the cell, the color of the PVA-SbQ(ARS) polymer layer instantly changed from pale yellow to reddish yellow indicating the formation of an ARS-Al(III) complex on the surface of the electrodes.

Because of the strong chelating ability of Alizarin Red S to Al(III), the ARS-Al(III) complex formed was irreversible<sup>[12]</sup>. Therefore, the decrease in current response was recorded and the current changes obtained were used to construct a calibration curve. An unused fresh PVA-SbQ(ARS)-SPCEs was used for each individual measurement. PVA-SbQ(ARS)-SPCEs were calibrated using Al(III) standard solution and calibration curves for Al(III) are shown in Fig. 6. Each point represents the mean value of 5 measurements and the error bars represent one standard deviation. The peak current change ( $i_p - i$ ) in Fig. 6, represents the difference between the current response obtained after addition of an Al(III) sample and the response of the blank. The detection

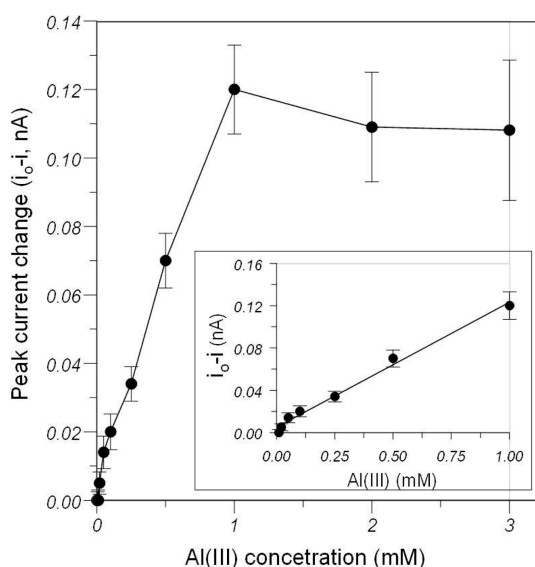


Fig. 6. Calibration curve for Al(III) using PVA-SbQ (ARS)-SPCEs. Inset: linear relationship between peak current and Al(III) concentration over the range of 0.05-1.0 mM.

limit (25  $\mu\text{M}$ ), sensitivity (3.8  $\text{nA}\mu\text{M}^{-1}\text{cm}^{-2}$ ) and linear range (25  $\mu\text{M}$  to 1 mM) of the method were determined using the results obtained. Intra-electrode reproducibility was determined as a coefficient of variation (CV) of less than 14.5 % over the Al(III) concentration range of 0.1 mM ~ 0.5 mM.

### 3.2. Comparison with Alternative Electrochemical Al(III) Detection Methods

The suitability of PVA-SbQ(ARS)-SPCEs for Al(III) detection in water samples was investigated in comparison with other methods using CMEs. The results are summarized in Table 1.

It was noted that the anodic peak currents obtained using the methods based on ASV (adsorption stripping voltammetry) in Table 1, were obtained by the reduction or oxidation of chelator-metal complexes that were accumulated on the surface of electrodes prior to application of the stripping potential. However, the system under investigation in this study detects the change in oxidation current produced not from the metallic complexes but from the modified chelator, ARS. Although all the methods summarized in Table 1 based on ASV show a lower detection limit compared with the present

Table 1. Comparison of present sensor system and other electrochemical Al(III) detection methods

Chelators used	Chelator Modification Method	Method based on	Detection limit (ppm)	Ref.
Alizarin Red	Polymerization with PVA-SbQ	Amperometry	167	Present system
Alizarin Red	Drop coating	ASV	60	[2]
Pyrocatechol violet	Adsorption	ASV	6	[11]
8-hydroxyquinoline	Adsorption	ASV	4	[12]

sensor based system, they usually need a longer detection time and a repeatable electrode polishing step at each measurement. Therefore, these differences indicate that the present system is a simpler system because it does not involve an analyte accumulation and an electrode polishing step and the use of the disposable electrodes. Furthermore, because of the additional steps of the ASV based methods, they may not be suitable for the incorporation into a hand held device.

Overall, in order to develop highly sensitive screen printed disposable sensor system for Al(III), the following approaches would be suggested; SPCEs could be modified using PVA-SbQ with chelators that have highly specific and strong chelating abilities to Al(III) such as N,N'-Bis(salicylidene)-1,2-phenylenediamine<sup>[5]</sup>. Another approach would be to incorporate chelators into the screen-printed carbon ink electrode in a manner similar to that described reported previously<sup>[13,14]</sup>. This may be easily achieved by mixing the chelator with the carbon ink prior to printing.

## 4. Conclusion

The work carried out in this study has demonstrated the use of a chelator for the on-site electrochemical determination of aluminum in water resources. Unlike traditional electrochemical detection methods such as ASV, the methods carried out in this work were based upon the measurement of changes in the electrochemical behavior of the chelator upon complexation with Al(III). The sensor developed in this study showed a detection limit for Al(III) of 25  $\mu\text{M}$  (167 ppm), with a short turnaround time (15 min for each measurement).

The simple screen-printing technique and the effective chelator modification procedure using direct polymerization on electrodes allows inexpensive and disposable amperometric Al(III) sensor fabrication.

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