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# DETERMINATION OF OXALATE ION IN BAYER LIQUOR USING ELECTROCHEMICAL METHOD

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## Abstract

The Bayer process can be summarized as the digestion of bauxite with caustic liquor and the subsequent precipitation of hydrated alumina [1]. Most bauxite contains organic compounds in various amounts. Depending upon the digestion conditions, 5–10% of the organic carbon is converted to sodiumoxalate [2]. When sodiumoxalate, if not controlled in Bayer process, builds up to a certain level of supersaturation, it precipitates out in the hydrate precipitator tank. This co-precipitation affects the quality of alumina [3].

In this study, we investigated the electrochemical determination of oxalate ion by using differential puls voltammetry in Bayer liquor. A linear relationship between oxalate concentration and current response was obtained with good reproducibility of the current.

## Introduction

The Bayer process can be summarised as the digestion of bauxite with caustic liquor and the subsequent precipitation of hydrated alumina [1]. Bauxite often contains organic matter in various amounts. Typically digestion of the bauxite during the Bayer process more than half of this organic carbon is extracted into the liquor. With recycling of the Bayer liquor the concentration of humic substances and their degration and oxidation products builds up an equilibrium concentration depending on the amount of organic carbon present in the bauxite. Because of this, in the Bayer process, the organic matter builds up to an equilibrium level, typically to 10–30 g/L of organic carbon content, determined by the outputs and the inputs [4]. Besides the bauxite input, some organic matter comes from other sources, such as process water, red mud flocculants or antifoams. The outputs are complex through the adsorption on the red mud or adsorption on the product. The accumulated organic matter and its breakdown products are known to cause numerous process problems. As a result, the liquors darken, and notable amounts of carbonate and oxalate are formed. Depending upon the digestion conditions, typically 5–10% of the organic carbon is converted to sodium oxalate [2, 3].

Sodium oxalate has been shown to be very harmful with regard to alumina productivity and particle size [3, 5]. When sodium oxalate, if not controlled, attains a certain level of supersaturation, it precipitates out as fine needles in the hydrate precipitator tank. This coprecipitation affects the alumina product quality and productivity in many ways [3].

A variety of techniques have been utilized for the identification and determination of sodium oxalate and organic substances in Bayer liquors, these have included titrimetry [6], ion chromatography [7–10], high performance liquid chromatograph [11–14], and gas chromatography [15–17]. In many factories, the oxalate was determined by titration with a standard potassium permanganate solution. This method often resulted in low precision and accuracy. Furthermore, it takes much time and many agents. Voltammetric techniques have not found use for this purpose. Recently, there has been a considerable effort in the development of voltammetric methods for the determination of some biological and industrial samples. It is generally believed that direct redox reactions of these species at the surface of usual electrodes are irreversible and therefore require high over-potential [18]. Moreover, the direct redox reaction of these species at the unmodified electrodes takes place at very similar potentials and often suffers from a pronounced fouling effect, which results in rather poor selectivity and reproducibility.

In this study, we investigated the electrochemical determination of oxalate ion at pencil graphite electrode (PGE) by using differential puls voltammetry in Bayer liquor. A linear relationship between oxalate concentration and current response was obtained with good reproducibility of the current . Also real Bayer process samples were analysed by DPV and the results obtained compared with titration by potassium permanganate.

## Experimental

### Chemical and Reagents

Sodium sulfate (99.0%, Aldrich), potassium permanganate (99.0%, Aldrich), and sodium oxalate (99.5%, Aldrich) reagents are commercially available as analytical grade and used without further purification. Stock solutions of oxalate solution were prepared daily from by using ultra-pure deinoized water. Bayer liquors and alumina hydrate were obtainaed from Seydişehir Eti Aluminyum A.Ş. (Turkey).

### Apparatus

Electrochemical experiments were carried out by a conventional three-electrode system. Pencil graphite (PG) was used as working electrode. Pt wire and saturated calomel electrode (SCE) were used as an auxiliary and reference electrode, respectively. Differential pulse voltammetry (DPV) measurements were performed by Autolab PGSTAT 100 Potentiostat/ Galvanostat with GPES 4.9 Version conversion software (EcoChemie, The Netherlands).

## Electrochemical Detection of Oxalate Ion

The electrochemical detection of oxalate ion was performed in aqueous solution of 0.1 M $Na_2SO_4$ using potential puls between 0.0 V and +1.5 V with a scan rate of 50 $mVs^{-1}$ for three scans. All electroanalytical measurement were made at room temperature.

## Result and Discussion

### Preparation of Calibration Curve for Oxalate Ion

A series of DPVs was recorded at various concentrations of oxalate to determine its calibration curve. The response of the PG electrode to oxalate was found to increase with increasing oxalate concentration. Fig. 1 shows DPV curves recorded on the PG electrode in the presence of various oxalate concentrations in the range of 0.10–10mM. Differential pulse voltammograms of oxalate had shown only a single peak (oxalate). The figure 2 shows the calibration curve obtained by measuring the DPV peak current intensity (in μA) vs. the concentration of oxalate (in mM) with a correlation coefficient of 0.9984.

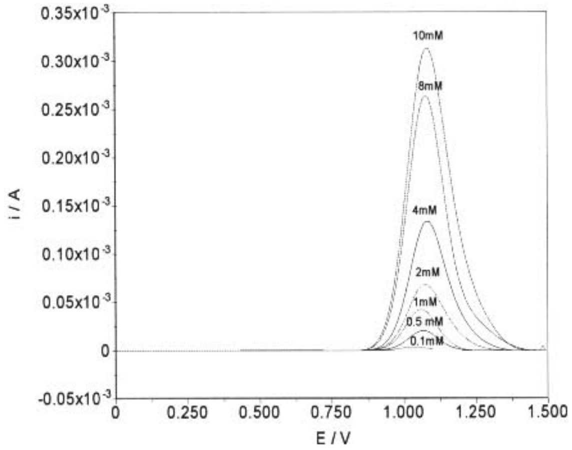

Fig. 1. .Differential pulse voltammograms of oxalate at various concentrations in 0.1 M $Na_2SO_4$ at the PGE. Scan rate was $50mVs^{-1}$.

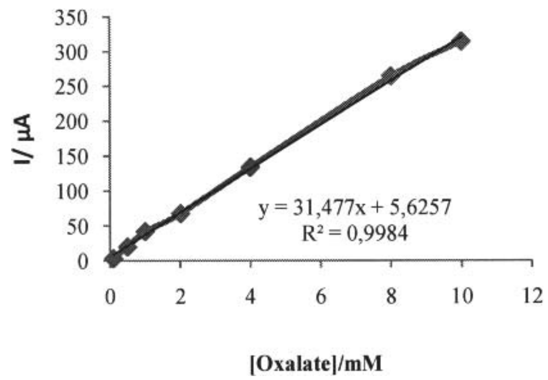

Fig. 2. The analytical curve is linear in the range 0.10–10.00mM of oxalate concentration with a correlation coefficient ($R^2$) of 0.9984.

### Real Sample Analysis

In order to verify the reliability of the electrode, it was applied for the determination of oxalate in Bayer liquors (pregnant liquor and spent liquor) and alumina hydrate samples. The oxalate concentrations in the samples were determined using the standard addition method and direct interpolation in the linear regression. Obtained results for oxalate ion concentrations from different Bayer liquors and alumina hydrate samples are given in Table I. Also oxalate in Bayer real samples determinated by using titration method. Obtained results are given Table 2

Table I. Experimental Results of Oxalate Ion

| **Samples** | **[Oxalate] with DPV** | **[Oxalate] with titration** |
|---|---|---|
| Pregnant liquor | 33792 mg/L | 48000 mg/L |
| Spent liquor | 21472 mg/L | 26000 mg/L |
| Hydrate alumina | 0.122 mg/g$_{sample}$ | 0.20 mg/g$_{sample}$ |

## Conclusion

Electrochemistry has many advantages for making it an appealing choice for industrial oxalate ion analysis. Electrochemical method is a high specific and analitical method which is likely to get preference in sampling small volumes and complex sample matrices. The determination of sodium oxalate in several Bayer samples was undertaken and the results have been summarised in Table 1. As can be seen compared to results, titration method is higher than DPV method. Because of titration method often resulted in low precision and accuracy.

In this study, PG electrodes was performed for the first time in different Bayer liquors and alumina hydrate. This method provide a simple and rapid technique to determine oxalate ion in high alkali media. Also, this method takes less time when compared with other methods. Further studies on the variations of electrode, electrolyte, linearity of response and quantitative properties of DPV method, etc. are underway. The developed method is straightforward and suitable for the determination of the oxalate ion in Bayer samples.

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