Electrochemical detection of As\textsuperscript{3+} and As\textsuperscript{5+} by anodic stripping voltammetry at a gold electrode

D T Lestarini and T A Ivandini

Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia

Corresponding author: ivandini.tri@sci.ui.ac.id

Abstract. In this article, electrochemical detection of arsenite (As\textsuperscript{3+}) and arsenate (As\textsuperscript{5+}) by stripping voltammetry at a gold electrode has been investigated. As\textsuperscript{3+} and As\textsuperscript{5+} are reduced to arsine (AsH\textsubscript{3}) in 0.1 M sodium borohydride before deposition on the electrode surface. 0.1 M HCl was used as the supporting electrolyte, where Cl\textsuperscript{−} ions act as an ionic bridge, facilitating reduction at the working electrode. As\textsuperscript{3+} and As\textsuperscript{5+} can be deposited as arsine by simple electrochemical reduction at \(-0.5\) V (versus Ag/AgCl). Anodic stripping voltammograms of arsine at a gold electrode showed similar peak potentials for As\textsuperscript{0} oxidation (\(\approx 0.31\) V versus Ag/AgCl). The stripping voltammograms for As\textsuperscript{3+} and As\textsuperscript{5+} presented similar peak shapes and current intensities. A reaction mechanism involving reduction to As\textsuperscript{0} at a mild potential in a strong acid, followed by oxidation of As\textsuperscript{0} to As\textsuperscript{3+} at the gold electrode, was proposed. The method developed offers a wide linear concentration range for As\textsuperscript{3+} (0–5 ppm) and As\textsuperscript{5+} (0–20 ppm) and very low limits of detection for As\textsuperscript{3+} (0.85 ppm) and As\textsuperscript{5+} (6.07 ppm).

Keywords: anodic stripping voltammetry, arsenic, arsenate, sodium borohydride, gold electrode.

1. Introduction

Arsenic is one of the most toxic elements encountered in the environment. It is commonly found in marine environments and is highly resistant to chemical degradation. Arsenic exists in four oxidation states (i.e., As\textsuperscript{3−}, As\textsuperscript{0}, As\textsuperscript{3+}, and As\textsuperscript{5+}), with As\textsuperscript{3+} and As\textsuperscript{5+} being the most widespread forms in nature [1]. Arsenic is mostly to be found in its inorganic form in the natural water, namely oxyanions of trivalent arsenite (As\textsuperscript{3−}) or pentavalent arsenate (As\textsuperscript{5+}). Arsenic can also exist in organic forms, such as monomethyl arsenic acid (MMA) and dimethylarsinic acid (DMA), which are less toxic, and in volatile organoarsenic species such as methylarsine (h (AsH\textsubscript{3}) [2].

These different arsenic species have very different toxicities. Their acute toxicity decreases in the order arsenic (AsH\textsubscript{3}) >> arsenite (As\textsuperscript{3−}) > arsenate (As\textsuperscript{5+}) >> dimethylarsinate > monomethylarsonate >> arsenobetaine and arsenocholine, both of which are organoarsenic compounds that are found in marine organisms and, therefore, seafood [3]. Arsine gas is formed when arsenic or arsenic-containing materials react with acids. It is often applied as dopant in the industry such as semiconductor and crystals manufacture for fiber optics and computer chips, and in lesser usage are for galvanizing, soldering, etching, burnishing, and lead plating. Arsine is highly toxic, and its threshold limit value, is only 10 µg/m\textsuperscript{3} [4].

Determination of arsenic is conventionally based on the Gutzeit method or inductively coupled plasma spectrometry [5]. However, electroanalytical methods of anodic stripping voltammetry (ASV) and differential pulse anodic stripping voltammetry exhibit an excellent sensitivity and allow the detection of arsenic in distinct oxidation states using low-cost portable equipment, making them ideal
for field analysis [6]. The determination of arsenic using ASV at a gold electrode was first investigated by Forsberg et al. [7] in 1975. They reported that reducing $\text{As}^\text{III}$ to $\text{As}^\text{V}$, which they achieved by heating with sodium sulfite ($\text{Na}_2\text{SO}_3$) in a concentrated acid solution, is necessary because $\text{As}^\text{V}$ is electroinactive [7].

ASV comprises two steps: (1) the analyte preconcentration or deposition by reduction process on an electrode surface; (2) the stripping process of preconcentrated analyte on the electrode surface by oxidation. Gold is the most suitable material for arsenic determination, due to the stable intermetallic compound of Au–As can be formed during the deposition stage [8,9]. Yamada et al. [8] have reported that inorganic $\text{As}^\text{III}$ and $\text{As}^\text{V}$ in mixed solutions can be detected at gold-modified boron-doped diamond electrodes by ASV at detection limits of 5 and 100 ppb, respectively.

In the present study, we developed and assessed an electrochemical sensor that is based on the reduction of inorganic arsenic using sodium borohydride to form arsine. An HCl solution is used as the electrolyte to provide the very low pH conditions under which arsenic can be reduced to $\text{As}^\text{III}$ at mild potentials [10]. A linear current response is observed within the range of concentration from 2–10 ppm. Moreover, the current response’s stability is demonstrated, as well as a feasible reaction mechanism.

2. Experimental

2.1. Chemicals and materials
Sodium arsenite ($\text{Na}_3\text{AsO}_3$), sodium arsenate ($\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$), hydrogen chloride (HCl), sodium borohydride (NaBH₄), and all other compounds (ACS-certified reagent grade) were obtained from Wako Co. and applied without further purification. Aqueous solutions were made in deionized water (Merck Millipore). Fresh solution of 0.1 M NaBH₄ was prepared daily.

2.2. Electrochemical measurements
Electrochemical measurements were performed in a room temperature with an ASV technique using an electrochemical cell completed with a magnetic stirrer. Gold plate (area of around 0.25 cm²) was used as the working electrode, while platinum spiral and Ag/AgCl were respectively employed as the counter and the reference electrodes. HCl solution (0.1 M) was used as the electrolyte and ED410 eDAQ e-corder was used as the potentiostat. All measurements were conducted with stirring at room temperature.

3. Results and discussion

3.1. Reduction of arsenite and arsenate to arsine
It was previously stated that the ASV method comprises the analyte preconcentration by reduction process on the electrode surface and the preconcentrated analyte is stripped on the electrode surface by oxidation [8]. Initially, $\text{As}^\text{V}$ or $\text{As}^\text{III}$ is reduced to $\text{As}^\text{III}$ with an adequately negative potential, and on the gold electrode surface, a film will be formed [6], via the following reactions:

$$\text{As}^\text{V} + 3\text{e}^- \rightarrow \text{As}^\text{III}$$

$$\text{As}^\text{V} + 5\text{e}^- \rightarrow \text{As}^\text{III}$$

In this study, ASV detection of arsenic was conducted on the basis of the reduction of arsenite and arsenate to arsine using sodium borohydride in acidic conditions; that is,

$$\text{As}^\text{V} + 2\text{BH}_4^- + 6\text{H}_2\text{O} \rightarrow \text{As}^\text{III} + 2\text{B(OH)}_3^- + 7\text{H}_2$$

$$\text{As}^\text{III} + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow \text{AsH}_3 + 3\text{B(OH)}_3^- + 9\text{H}_2$$
At the stripping step, arsenic is oxidized to As\(^{5+}\). Two mechanisms are proposed for this oxidation reaction. The first mechanism involves a two-step oxidation process where AsH\(_3\) is oxidized to As\(^{3+}\), further to As\(^{5+}\) through an electrochemical oxidation at the gold electrode, as shown by the below equations:

\[
\begin{align*}
\text{AsH}_3 & \rightarrow \text{As}^{0} + 3\text{H}^+ + 3e^- \\
\text{As}^{0} & \rightarrow \text{As}^{3+} + 3e^- 
\end{align*}
\]

The second proposed mechanism involves the direct oxidation of AsH\(_3\), to As\(^{3+}\). Preliminary ASV experiments showed that the optimum peak oxidation currents for As\(^{3+}\) and As\(^{5+}\) are achieved by maintaining the potential at \(-0.5\) V (versus Ag/AgCl) (figure 1 and figure 2).

### 3.2. ASV conditions for As\(^{3+}\)

In order to achieve the optimal conditions for As\(^{3+}\), we investigated the deposition potential \(E_d\), deposition time \(t_d\), and scan rate. A deposition of \(-0.5\) V (versus Ag/AgCl) was applied for As\(^{3+}\) as this potential has been previously reported to be optimal [11]. A 60 s deposition time resulted the highest signal-to-background (S/B) ratio for ASV conducted in 0.1 M HCl. The deposition time is the time required to reduce As\(^{3+}\) to As\(^{5+}\) at the electrode surface. At low concentrations, longer deposition is required for the detection of As\(^{3+}\), while at high concentration of As\(^{3+}\), short deposition times is to be applied in order to prevent saturation of the electrode surface [12]. HCl was used as the electrolyte, because Cl\(^-\) ion serves as an ionic bridge between the working electrodes to facilitate their reduction. The polarograms for As\(^{3+}\) in acidic media present two waves [6].

The scan rate parameters were also optimized. The correct scan rate must be applied to completely strip all the deposited As\(^{3+}\). At low scan rate, the deposited As\(^{3+}\) is also stripped, however will result in a poor current response. Conversely, a high scan rate results in a higher current, however should the scan rate be too high, the stripping process will not be completely occurred on the deposited As\(^{3+}\) leads to a distortion of the peak shape [8]. The optimum ASV conditions for As\(^{3+}\) were found to be \(E_d = -0.5\) V, \(t_d = 60\) s, and scan rate = 200 mV/s. The background-subtracted stripping voltammograms and the related linear calibration curve \((r = 0.97)\) are shown in figure 1. Limit of detection (LOD) of 0.85 ppm was estimated.

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**Figure 1**: Background-subtracted voltammograms of 0.1 M HCl solutions containing of 0.1 M NaBH\(_4\), and various concentrations of As\(^{3+}\) (0–50 ppm). Stripping voltammetry parameters were \(E_d = -0.5\) V, \(t_d = 60\) s, and scan rate = 200 mV/s. The inset shows the linear calibration curve extracted from the related stripping voltammograms.

![Background-subtracted voltammograms](image-url)
As solution to be oxidation of As

Detection of 

4.

Figure 2. Background-subtracted stripping voltammetry for various concentrations of As\(^{3+}\) (0–20 ppm) in 0.1 M HCl solutions using 0.1 M NaBH\(_4\). Stripping voltammetry parameters were \(E_{sw} = -0.5\) V, \(t_{sw} = 60\) s, and scan rate = 200 mV/s. The inset shows the linear calibration curve extracted from the related stripping voltammograms.

3.3. ASV conditions for As\(^{3+}\)

As\(^{3+}\) deposition requires a very low negative potential in order to resolve the high activation energy of As\(^{3+}\) reduction. Nevertheless, at high negative potentials, evolution of hydrogen can occur, and the formed hydrogen could be adsorbed on the electrode surface, inhibit the As\(^{3+}\) deposition [8]. Conversely, the application of very low potentials can also lead to the generation of hydrogen gas by water reduction. In a previous study, the adsorption of hydrogen gas was minimized by controlling the deposition of As\(^{3+}\) in two steps, including the reduction step to be As\(^{5+}\) followed by the reduction of As\(^{5+}\) to be As\(^{3+}\) [8]. In that work, the direct deposition of As\(^{3+}\) was predict to occur at a potential of \(-1.5\) V (versus Ag/AgCl).

In the present study, ASV detection of As\(^{3+}\) was performed on the basis of the reduction of arsenate to arsine with sodium borohydride. Followed by its deposition on a gold electrode at a potential of \(-0.5\) V (versus Ag/AgCl). Reduction of arsenate to arsine was performed in order to avoid the need for a very low negative potential. The preconcentration of As\(^{3+}\) was proposed to comprise two steps, including the reduction of As\(^{3+}\) to arsine and deposition to be As\(^{5+}\) on the electrode surface, whereas the stripping step was based on the oxidation of As\(^{5+}\) to As\(^{3+}\). The background-subtracted stripping voltammograms and linear calibration curve \((r = 0.90)\) with estimated LOD of 6.07 ppm as shown in figure 2. The optimal stripping voltammetry conditions for As\(^{3+}\) were found to be \(E_{sw} = -0.5\) V, \(t_{sw} = 60\) s, and scan rate = 200 mV/s.

4. Conclusions
Detection of As\(^{3+}\) and As\(^{5+}\) was successfully achieved using ASV. As\(^{3+}\) can be deposited by the reduction of As\(^{5+}\) to arsine and subsequently detected via two-step oxidation (arsine to As\(^{5+}\), followed by As\(^{5+}\) to As\(^{3+}\)). For As\(^{5+}\), the deposition step was based on the reduction of As\(^{5+}\) to As\(^{3+}\), followed by the reduction of As\(^{3+}\) to arsine, whereas the stripping step was based on the oxidation of arsine to As\(^{5+}\), followed by oxidation of As\(^{5+}\) to As\(^{3+}\). The optimum deposition potential, deposition time, and scan rate were found to be \(-0.5\) V, 60 s, and 200 mV/s, respectively. Good linear responses were observed for standard solutions of As\(^{3+}\) and As\(^{5+}\). Using our method, detection limits of 0.85 and 6.07 ppm can be achieved for As\(^{3+}\) and As\(^{5+}\), respectively.
Acknowledgements
This work was funded by PITTA Grant Universitas Indonesia with contract number 1822/UN2.R3.1/PPM.00.01/2017. The authors would like to thank Einago (www.einago.com) for the English language review.

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