Anodic stripping voltammetry of inorganic species of \( \text{As}^{3+} \) and \( \text{As}^{5+} \) at gold-modified boron doped diamond electrodes

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Abstract

Electrochemical detection of mixture solutions of \( \text{As}^{3+} \) and \( \text{As}^{5+} \) has been investigated by stripping voltammetry at gold-modified diamond electrodes. The method was performed based on stripping oxidation of \( \text{As}^0 \) deposited at the electrode surface. Whereas \( \text{As}^{3+} \) can be deposited by simple electrochemical reduction of \( \text{As}^{3+} \) to \( \text{As}^0 \) at \(-0.4 \, \text{V} \) (vs. Ag/AgCl), much higher potential is required to overcome the activation energy of \( \text{As}^{5+} \) reduction. However, in such a high potential, hydrogen evolution also occurs. Consequently, one more step should be added to release the hydrogen gas adsorbed at the electrode surface during the reduction step. During the deposition of \( \text{As}^{5+} \), \( \text{As}^{3+} \) species was also simultaneously deposited. Therefore, to differentiate \( \text{As}^{3+} \) and \( \text{As}^{5+} \) quantification in a mixture solution, both stripping voltammetry methods should be performed and calculated mathematically. Comparison of stripping voltammograms of both methods for \( \text{As}^{3+} \) solution in the absence of \( \text{As}^{5+} \) demonstrated similar peak shapes and current intensities, confirming that error calculation of \( \text{As}^{5+} \) concentration in the mixture solution with \( \text{As}^{3+} \) can be avoided. Good linear responses were observed for each standard solution of \( \text{As}^{3+} \) and
As$^{5+}$. Linear calibration curve could also be achieved for a series concentrations of 100–1000 ppb As$^{5+}$ in a mixture solution with 100 ppb As$^{3+}$ ($r^2 = 0.99$) and for a series concentrations of 5–30 ppb As$^{3+}$ in a mixture solution with 100 ppb As$^{5+}$. Detection limits of 5 and 100 ppb can be achieved for As$^{3+}$ and As$^{5+}$ in a mixture solution, respectively. The reproducibility was shown for stripping voltammetry of As$^{3+}$ and As$^{5+}$ with an RSD ($n = 8$) of 7.5% and 8.4%, respectively. Good stability of gold-modified diamond electrodes before and after arsenic detection was also evaluated by SEM image. Application of the method for real sample analysis was performed for arsenic detection in Yokohama tap water.

**Keywords:** Total inorganic arsenic; Differentiation method; Stripping voltammetry; Gold; Diamond electrodes

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