# Chapter 81
# An Electrochemical Sensor for Trace Inorganic Arsenic Based on Nanoelectrode Ensembles

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**Abstract** The results of a study on the determination of trace levels of arsenic with nano-electrode ensembles (NEEs) are reported. The method is characterized by detection limit as low as 5 ng/L (65 pM) after 3 min preconcentration at −0.4 V. NEEs were applied to trace As analysis in real samples such as certified seawater samples.

## Introduction

In 1993, the World Health Organization (WHO) set to 10 μg/L the maximum limit for As concentration in drinking water. As a consequence, there is a real need for simple and reliable analytical methods able to reach this low detection limit, being, at the same time, suitable for decentralized analysis even in remote areas. Recent papers [1, 2] showed that the stripping voltammetric (ASV) determination of arsenic can be improved by nanostructuring the electrode surface. In particular, several papers described the successful use of carbon electrodes modified with gold nanoparticles (Au-Nps) for trace arsenic analysis. The Au-Nps can be deposited by

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mean of electroless [3] or electrochemical methods [4, 5]. The so prepared modified electrodes showed detection limit (DL) of 0.01 μg/L [1].

Arsenic toxicity is a function of its speciation; as far as the oxidation state is concerned it is known that As(V) is 100 times less toxic than As(III) [6].

In order to try to further improve the reliability and analytical performances of the ASV determination of trace arsenic, in the present work we examine the possibility to exploit the improved electroanalytical performances of the so called nanoelectrode ensembles (NEEs). It was indeed demonstrated that, thanks to dramatically improved signal to background current ratio and enhanced diffusion [7], NEEs can be successfully applied to trace analysis of a variety of redox analytes ranging from small organics [8] to large redox proteins and antigens [9], from antibiotics [10] to iodide [11].

In the present work we examine the use of NEEs for the anodic stripping analysis of inorganic arsenic focusing, in particular, on the optimization of the analytical conditions in order to lower the DL and improve the analytical performance.

# Experimental

## *Materials*

Polycarbonate filtration membranes (SPI-Pore, 47 mm filter diameter, 6 μm filter thickness, $6 \times 10^8$ pores/cm$^2$) with a nominal pore diameter of 30 nm were used as the templates to prepare the NEEs.

NEEs were prepared using the electroless plating procedure and assembled using a previously described procedure [7] and following modifications [12] As(III) stock solutions (100 mg/L) were prepared by dilution of a 0.05 mol/L standard NaAsO$_2$ solution (Carlo Erba). As(V) stock solutions (1,000 mg/L) were prepared from a 1,000 mg standard commercial solution of As$_2$O$_5$ (tritisol® – Merck). All other solutions were prepared with ACS grade reagents.

CASS-4 certified reference seawater standard was provided by the Canadian National Research Council. The certified concentration of As is $1.11 \pm 0.16$ μg/L.

## *Procedures*

### Determination of As(III)

0.33 mL of 6 M HCl + 65 mg hydrazine dihydrochloride were added to 10 mL of water (or to 10 mL of diluted certified reference solution). ASV measurements were performed as follows: (1) accumulation at −0.4 V performed for the desired time under continuous stirring; (2) 15 s equilibration in quiet solution; (3) SWV stripping from −0.40 to 0.45 V at 250 Hz frequency, square wave amplitude 75 mV, scan increment 12 mV.

### Determination of As(V)

50 mL of As(V) solution, 1.9 mM hydrazine and 4.9 mM of cysteine were added to a volumetric flask and heated at 80 °C in a water bath for 30 min under continuous stirring. After cooling to room temperature the solution was analyzed with the same procedure used for As(III).

## Results and Discussion

### AS-SWV of As(III) at NEE

For the determination of trace level of arsenic, we chose to operate with NEEs using anodic stripping-square wave voltammetry, AS-SWV. Preliminary experiments indicated that a deposition time between 120 and 180 s gives good results, the final choice depending on the concentration of the analyte. At longer deposition times we observed a decrease in the reproducibility of the stripping peak current and shorter linear range. This fact is explained taking into account a saturation effect of the available Au surface of the nano-sites of the NEE.

The increase of As(III) concentration above 8–10 µg/L causes the progressive lowering of the sensitivity up to a saturation effect; by decreasing the deposition time to 120 s, the sensitivity decreases, but the linear range increases.

Figure 81.1a shows the SW-ASV recorded at a NEE in 0.2 M HCl, 62 mM hydrazine, spiked with increasing amounts of As(III). A very sharp stripping peak is recorded at 0.0 V, with peak current that scales linearly for concentrations between 0.2 and 3.0 µg/L (see inset).

For comparison, Fig. 81.1b shows the AS-SWVs at a $Au_{macro}$ electrode recorded at As(III) concentrations from 20 to 150 µg/L, which shows that the stripping peak shifts to slightly more positive potential values, with much larger half-peak width (approximately 120 mV). Note that below 20 µg/L at this electrode the stripping peak is barely distinguished from the background.

Table 81.1 compares the analytical parameters obtained with a NEE and a $Au_{macro}$. NEEs furnish the best DL, which is among the lowest in comparison with the recent literature [11, 12, 13–15]. The $Au_{macro}$ is characterized by a much higher DL, but wider linear range. This behavior agrees with the hypothesis of the saturation of the gold nano-sites that occurs for the NEE: the larger is the available gold surface, the wider results the linear range.

### Redox State Speciation and Certified Sample Analysis

Preliminary experiments performed with $Au_{macro}$ electrode confirmed the completion of the reduction of As(V) to As(III) using cysteine as the reducing agent, under the conditions described in the experimental section. It was observed indeed that
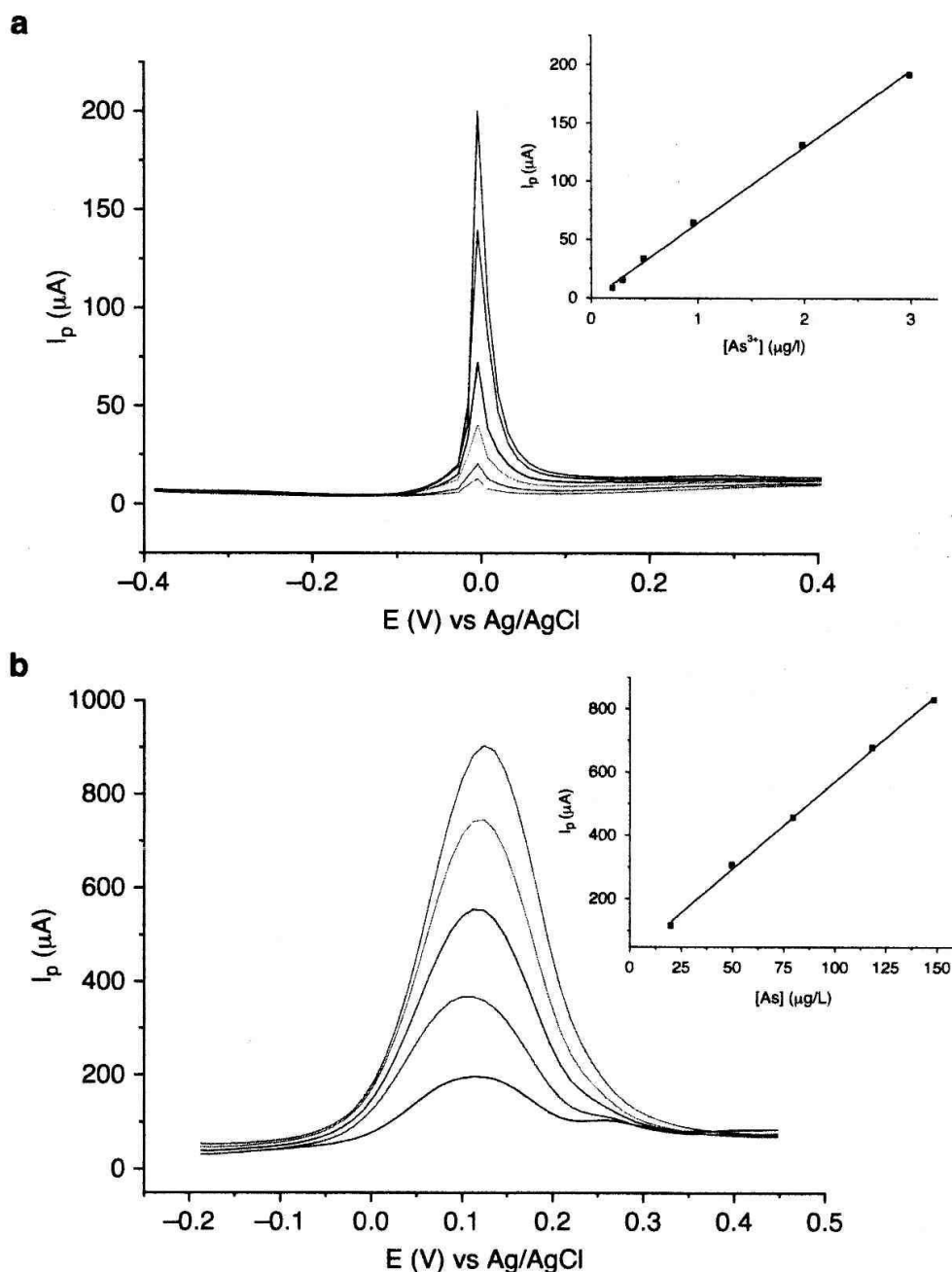
**Fig. 81.1** **a**) SW-ASVs at NEE in 0.2 M HCl at different As(III) concentrations (from 0.2 to 3.0 µg/L). *Inset*: relevant calibration plot. **b**) SW-ASVs recorded at Au$_{macro}$ electrode at increasing concentration of As(III): 20, 50, 75, 125 and 150 µg/L. *Inset*: relevant calibration plot. Other parameters as in Fig. 81.1

**Table 81.1** Comparison of the AS-SWV performances of NEE and Au$_{macro}$ electrode for the As(III) determination (deposition time 180 s)

|  | NEE | Au$_{macro}$ |
|---|---|---|
| DL | 0.005 g/L | 0.75 µg/L |
| LR | 0.2–6 µg/L | 20–150 µg/L |
| Sensitivity (m) | 65.57 µA×L/µg | 551 µA×L/µg |
| $\sigma_b$ | 0.11 µA | 1.38 µA |

*DL* detection limit calculated as DL = $3\sigma_b$/m, where σb is the standard deviation of the blank, *LR* linear range

AS-SWVs performed on equimolar concentration of As(III) generated by in situ chemical reduction of As(V), and As(III) added directly as $NaAsO_2$ give exactly the same voltammetric peaks, with calibration plots displaying the same sensitivity.

The above-developed method was tested for the determination of As in CASS-4. After reduction with cysteine (see section "Determination of As(V)"), 5 mL of CASS-4 were diluted 1:1 with HCl (final concentration 0.2 M) and adding hydrazine dihydrochloride (62 mM). The AS-SWV is characterized by a peak at 0.0 V versus Ag/AgCl which increases linearly after standard addition of As(III). The sample concentration, calculated by extrapolation of the calibration plot (not shown) and considering the dilution factor, was $1.18 \pm 0.06$ µg/L. This value is in satisfactory agreement with the value of $1.11 \pm 0.16$ µg/L declared by the National Research Council of Canada.

## Conclusions

In the present work we demonstrate that NEEs present better performance than gold macro electrodes and are competitive with respect to other nanostructured gold electrodes for the determination of inorganic As.

The obtained results indicate that the use of NEEs is advantageous when the solution concentrations of As are below 10 µg/L. Because of surface saturation effects the lowering of the dynamic range observed at NEE makes them less suitable for analysis at concentrations higher than 20 µg/L, where however also Au-macro electrodes can be successfully applied.

The proposed electrodes and procedures showed very good results also when applied to trace As analysis in real samples such as standard seawater.

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