

# Microdisc Arrays for Trace Analysis of Arsenic in Water

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Trace arsenic was measured by square wave anodic stripping voltammetry using gold microdisc array electrodes. A good linearity in 0–100 ppb concentration range and a detection limit lower than 1 ppb was obtained for  $\text{As}^{\text{III}}$ , with a measurement time of less than three minutes. Results for  $\text{As}^{\text{V}}$  indicated two linear slopes in the 0–40 ppb and 40–100 ppb ranges with a 2 ppb detection limit.

Arsenic is well known to be acutely toxic. The current maximum limit in drinking water is set at 50 ppb (part per billion or microgram per liter), but recently the World Health Organization (WHO) lowered the recommended maximum value to 10 ppb. Usual methods for trace arsenic detection are based on laboratory techniques such as inductively coupled plasma-mass spectrometry (ICP-MS). Faster and less expensive methods are however urgently needed to cover the growing needs of arsenic analysis. Anodic stripping voltammetry (ASV) provides a potential alternative approach. ASV is based on the preconcentration of the analyzed metals by reduction onto an electrode followed by an anodic reoxidation (stripping). This method has high accuracy and sensitivity (sub ppb). Being susceptible to miniaturization, it is particularly suited for cost-effective field measurements [1].

Microelectrode advantages for heavy metal analysis by ASV are well known, including a reduced noise level and a high diffusion transfer towards the electrode therefore eliminating the need for stirring during the concentration step. Arrays of microelectrodes integrated on silicon chips keep single microelectrode attractive properties while enhancing the sensor response by more than two orders of magnitude [2].

$\text{As}^{\text{III}}$ , the most toxic specie, was evaluated first, measurements being done in As spiked HCl solutions. The sensing electrode is an array of 135 gold discs, 10  $\mu\text{m}$  in diameter and separated by 300  $\mu\text{m}$ , integrated on a silicon chip. A number of parameters, including HCl concentration, pre-concentration potential and time and the stripping procedure (direct, differential pulse or square wave forms) were studied and optimized. Figure 1 shows the measured stripping peaks and the resulting calibration plot under optimized conditions (0.2 M HCl, preconcentration: 120 s/–0.3 V – no stirring, anodic square wave stripping: steps 8 mV – 50 Hz, amplitude 50 mV).

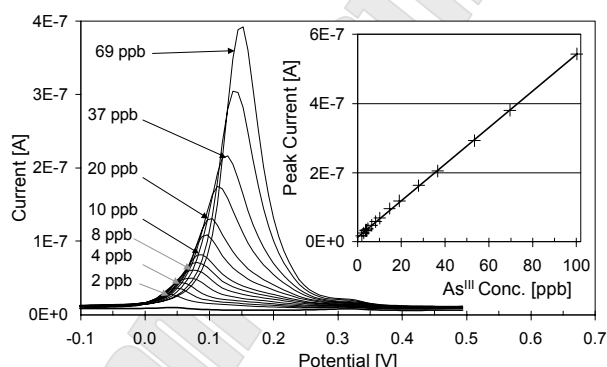


Figure 1:  $\text{As}^{\text{III}}$  in 0.2 M HCl; stripping peaks and calibration curve

Reproducible measurements and detection limit lower than 1 ppb can be achieved within a measurement time of less than three minutes. The linearity is very good up to ~100 ppb (correlation coefficient 0.9997). After monolayer coverage of gold

by arsenic the efficiency of the pre-concentration step decreases significantly. For higher As concentrations pre-concentration times must therefore be decreased.

Arsenic also exists in the  $\text{As}^{\text{V}}$  state under natural conditions.  $\text{As}^{\text{V}}$  is however more difficult to deposit due to the very cathodic potential necessary to reduce  $\text{As}^{\text{V}}$  to  $\text{As}^0$  (lower than –0.7 V versus Ag/AgCl/KCl 3 M).

Results obtained so far indicate two linearity ranges, 0 to 40 ppb and 40 ppb up to 100 ppb, where the curves are linear with a correlation coefficient 0.987 (Fig. 2) in these two ranges. The  $\text{As}^{\text{V}}$  detection limit is estimated at 2 ppb. More work will be necessary to improve these results, possibly by using a diamond microelectrode array instead of a gold array.

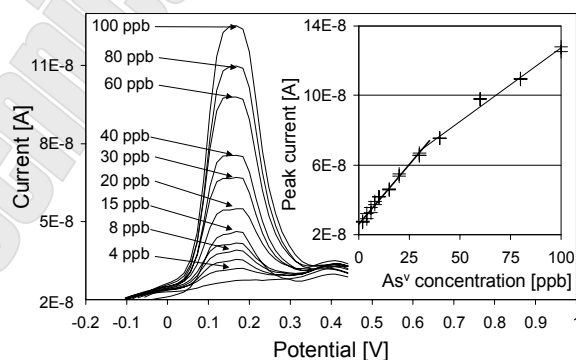


Figure 2:  $\text{As}^{\text{V}}$  in 2 M HCl; stripping peaks and calibration curve

In conclusion, a fast and sensitive method was obtained for  $\text{As}^{\text{III}}$  detection on gold microdisc arrays. Total As can also be obtained with this method using a suitable chemical reduction step before analysis. Direct analysis of  $\text{As}^{\text{V}}$  shows promising results, but needs further developments.

The acquired knowledge will possibly be exploited through development projects with external partners.

[1] K.Z. Brainina, N.A. Malakhova, N.Y. Stojko, "Stripping Voltammetry in Environmental and Food Analysis", Fresenius Journal of Analytical Chemistry, 368 (2000) 307

[2] J. Herdan, R. Feeney, B. Darling, "Field Evaluation of an Electrochemical Probe for in Situ Screening of Heavy Metals in Groundwater", Environmental Science & Technology, 32 (1998) 131