

Adsorptive Stripping Analysis of Trace Nickel at Iridium-Based Ultramicroelectrode Arrays

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Abstract

Lithographically fabricated iridium-based mercury microelectrode arrays are shown to be very suitable for adsorptive stripping measurements of trace nickel in the presence of the dimethylglyoxime complexing agent. Variables affecting the response have been assessed and optimized. The sensor optimization has resulted in a favorable and highly stable response, with good linearity and precision (RSD = 1.7%), and a low detection limit (0.5 µg/L with 30 s adsorption). Such adsorptive stripping performance makes the iridium-based microelectrode array very attractive for on-site measurements of trace metals that cannot be plated electrolytically.

Keywords: Nickel, Iridium microelectrode arrays, Adsorptive stripping analysis

1. Introduction

Stripping analysis is a powerful electroanalytical technique for trace metal measurements [1]. The power and scope of stripping analysis has been greatly enhanced during the past two decades owing to the introduction of adsorptive stripping protocols [2, 3] and microfabricated electrode arrays [4–6]. The latter were developed for amplifying the stripping signals while maintaining the attractive behavior of ultramicroelectrodes. In particular, iridium-based arrays have benefited from the low solubility of iridium in mercury and its good wettability. The attractive properties of mercury-coated iridium microelectrode arrays have been demonstrated previously in connection to conventional anodic stripping measurements of electrolytically-plated heavy metals (such as lead, cadmium, or copper). The suitability of such arrays for adsorptive stripping measurements of metals that cannot be deposited has not been documented.

The goal of this article is to combine the above advances by performing adsorptive stripping analysis at mercury-coated iridium-based microelectrode arrays. Such coupling is illustrated below in connection to measurements of trace nickel based on the adsorptive collection of its dimethylglyoxime (DMG) complex. Such adsorptive stripping measurements of the Ni-DMG complex are commonly performed at the hanging mercury drop [7, 8] or mercury-coated glassy-carbon [9] electrodes. Results of detailed optimization and characterization of this adsorptive stripping procedure at the iridium-based microelectrode array, presented in the following sections, indicate great analytical promise.

2. Experimental

2.1. Apparatus

Potentiometric stripping analysis (PSA) was carried out with a TraceLab system (PSU 20, Radiometer Inc., Denmark) in con-

nection with an IBM PS/55SX computer. Square-wave stripping voltammetric experiments were performed with AutoLab Electrochemical Instrument (PGSTAT 10, Eco Chemie B.V., The Netherlands). A Nikon A4-B Microscope was used to check the electrode quality. The electrochemical cell consisted of the iridium-based mercury-coated ultramicroelectrode array (Ir/HgU-MEA) as working electrode, a silver/silver chloride reference electrode (Model RE-1, BAS) and a platinum wire as counter electrode.

Fabrication of the IrUMEA chips was performed at the IBM, T. J. Watson Research Center (Yorktown Heights, NY). A 5000 Å oxide layer was thermally grown on a standard five-inch silicon wafer. After patterning, sequential electron beam evaporation steps were used to deposit a 100 Å Ti adhesion layer, a 2000 Å Ir layer, and a 5000 Å Au layer to be used for bonding pads. Iridium deposition was performed at an elevated temperature to reduce the tensile stress in the film. This is a crucial step, since improper deposition promotes cracking and flaking of the Ir surface. A second layer of Ti was deposited on top of the metal to insure adhesion to the insulating layer. Photolithographic stenciling was used to outline the ultramicroelectrode pattern and an Ar⁺ ion beam etch was used to transfer the stencil. Reactive RF-diode sputter deposition was used to deposit a 5000 Å SiO₂ insulating layer. Reactive ion etching was used to remove the SiO₂ in the desired pattern for the UME array and the bond pad. Additionally, an Ar⁺ ion beam was used to remove the top titanium layer on the top surface to expose the disks and the bond pad. There are 564 individual 10 µm diameter UMEs per array separated by 68 µm (center-to-center) and one array per chip, giving a total electroactive surface area of $6.37 \times 10^{-4} \text{ cm}^2$.

The wafer was cleaned and diced into 3.4 × 3.1 mm chips that were then glued onto a custom designed printed circuit board (CFC, Waltham, MA) with epoxy (EpoTek 905, Epoxy Technology, Billerica, MA). Electrical connection between the chip and the circuit board was made by a 1.25 µm Au wire (99.99% Williams Advanced Materials, Buffalo, NY). The epoxy (Orion Research, Inc. Beverly, MA) was applied around the chip to

insulate and protect the Au wire and the PC board from the solution. After application, the epoxy was cured for 2 hours at 50 °C.

2.2. Reagents

The 10 mg/L nickel solution was prepared daily by diluting the 1000 mg/L nickel (Atomic Absorption Standard, Aldrich) with water. The dimethylglyoxime (DMG) stock solution (Aldrich) was prepared in ethanol. The mercury plating solution consisted of 1600 mg/L mercury perchlorate in 0.008 M HClO₄. An ammonia buffer solution (0.05 M, pH 9.2) served as the supporting electrolyte. A 1 M potassium thiocyanate (Aldrich) solution was used for the cleaning the iridium-based mercury electrode. All chemicals used were of analytical grade. Aqueous solutions were made with deionized water.

2.3. Procedure

Mercury was deposited on the iridium-based ultramicroelectrode arrays according to an earlier protocol [4]. The nickel-containing ammonia buffer sample, containing 2×10^{-5} M DMG, was added to the electrochemical cell and stirred. A potential of -1.3 V (vs. Ag/AgCl) was applied (for 1 s) to 'clean' the electrode. The adsorption potential (usually -0.2 V) was applied subsequently for a short duration (5–30 s) for accumulating the Ni-DMG complex on the electrode surface. Following a 5 s rest period, potentiometric stripping was carried out with a constant current of -4 μ A until reaching the final potential of -1.20 V. The procedure was repeated after a 1-s 'cleaning' at -1.30 V, and a standard addition of nickel. Square-wave adsorptive stripping experiments were carried in a similar fashion using a frequency of 100 Hz of frequency and a 60 mV amplitude. All experiments were carried out in the presence of oxygen and at room temperature, unless indicated otherwise.

3. Results and Discussion

Adsorptive stripping measurements of nickel, and other trace metals, are commonly carried out at the hanging mercury electrode that offers a smooth uniform surface for optimal adsorption. Glassy carbon electrodes, coated with thin mercury films, are also being used for adsorptive measurements of nickel [9]. Figure 1 compares the adsorptive stripping potentiometric response of mercury-coated glassy-carbon (A) and iridium array (B) electrodes to 20 μ g/L (ppb) nickel following a 10 s accumulation. Examination of the raw data (a) clearly indicates that the iridium microelectrode array offers a more defined nickel peak ($E_p = -1.020$ V), with improved signal-to-background characteristics. Similar response characteristics are observed following the powerful data processing (noise filtration and baseline fitting) inherent to computerized stripping potentiometry. As will be illustrated in the following sections, the iridium array offers also a substantial improvement in the stability of the adsorptive stripping response.

The stripping mode has a profound effect upon the adsorptive stripping response of the iridium-microarray sensor. Figure 2 compares the voltammetric (A) and potentiometric (B) stripping response to a nondearated 50 μ g/L nickel solution. The larger background of the square-wave voltammetric mode results in

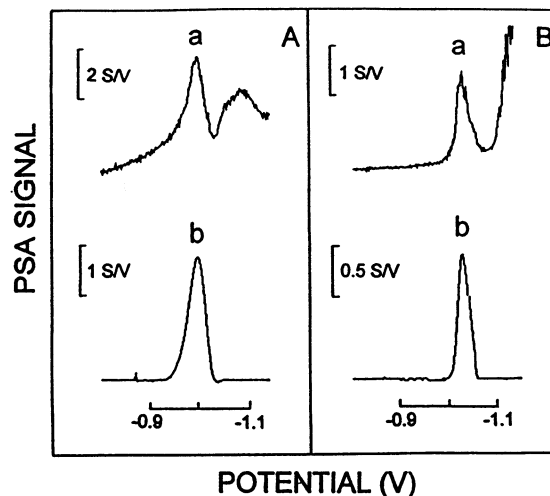


Fig. 1. Comparison of the adsorptive stripping potentiometric signal for 20 μ g/L of nickel at the mercury-coated glassy-carbon (A) and iridium-based mercury (B) electrodes. a) Before filtration and baseline fitting; b) after filtration and baseline fitting. Accumulation for 10 s at -0.20 V, following by a chronopotentiometric stripping with a current of -4 μ A. An ammonia buffer (0.05 M pH 9.2) solution, containing 2×10^{-5} M DMG, was used as the electrolyte.

inferior signal-to-background characteristics (a, A vs. B). Yet, both techniques offer similar response characteristics following the baseline fitting (b). Overall, the data of Figures 1 and 2 clearly illustrate that the iridium-based microelectrodes offer convenient adsorptive stripping measurements of trace nickel in connection to short adsorption times and nondearated samples.

Various parameters influencing the adsorptive stripping potentiometric response at the mercury-coated iridium microelectrode array were investigated and optimized. Figure 3A illustrates that the nickel signal increases rapidly upon raising the ligand concentration between 0 and 8×10^{-6} M, and levels off above 1×10^{-5} M DMG. The response increases gradually upon

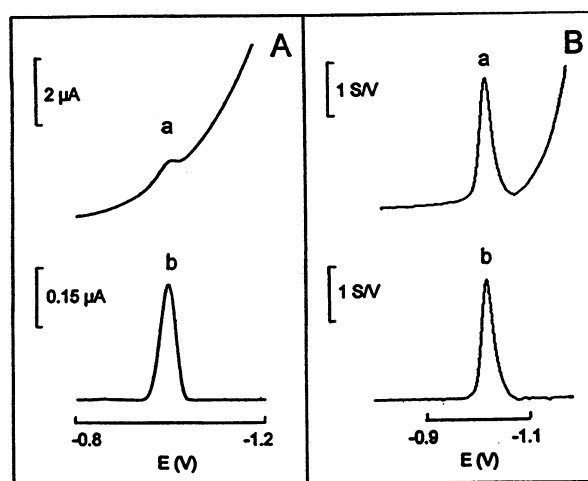


Fig. 2. Square-wave stripping voltammograms (A) and stripping potentiogram (B) for 50 μ g/L nickel at the mercury-coated iridium ultramicroelectrode array. a) original curve; b) after baseline fitting. Square-wave stripping with 100 Hz frequency and 60 mV amplitude. A constant current of -5 μ A was used in the stripping potentiometric measurements. Accumulation for 10 s at -0.2 V. Other conditions, as in Figure 1B.

changing the adsorption potential between -0.05 and -0.20 V, decreases gradually between -0.20 V and -0.40 V, and then more slowly (Figure 3B). The nickel peak increases rapidly upon changing the accumulation time between 0 and 4 s, and nearly levels off for longer accumulation periods (Figure 3C).

Figure 4A illustrates the stability advantage of the iridium-based mercury sensor array over the mercury-coated glassy carbon electrode. The coated carbon electrode displays a gradual decrease of its nickel peak (to 82% of its original value) during these 35 repetitive runs. In contrast, a highly stable response is observed at the iridium-based array over the entire period. Unlike the common use of the mercury electrode, the surface of the sensor array is not renewable between successive runs. Adsorptive stripping applications would require proper attention to the complete desorption of the complex prior to each run. A short (1 s) 'cleaning' step at -1.30 V is sufficient to erase memory effects in connection to the Ni-DMG system. This is illustrated from a carry-over experiment, involving sequential measurements (of four replicates) of 5 and 20 $\mu\text{g/L}$ nickel solutions, using the same mercury-coated surface (Figure 4B). The sensor array responds rapidly to sudden changes in the nickel level. The peak rises rapidly from the 5 $\mu\text{g/L}$ baseline upon transferring the sensor to the 25 $\mu\text{g/L}$ solution, and decays rapidly upon returning to the original low-concentration medium.

While the adsorptive stripping potentiometric data reported above have been obtained in the presence of dissolved oxygen, such use of aerated nickel solutions requires a judicious selection of the constant stripping current. Figure 5A compares the effect

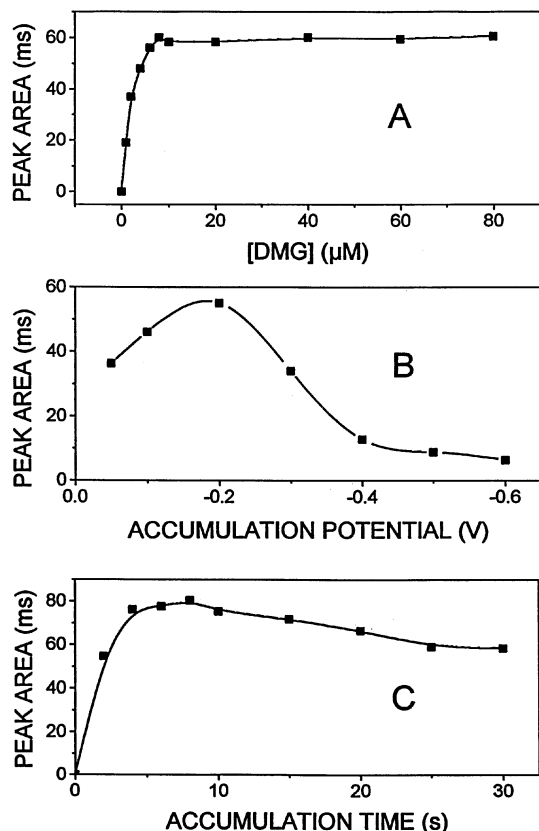


Fig. 3. Effect of the ligand concentration (A), accumulation potential (B), and accumulation time (C) upon the stripping potentiometric response for 10 $\mu\text{g/L}$ nickel. Accumulation for 10 s at -0.2 V, with a subsequent stripping using a current of -4 μA . Other conditions, as in Figure 1B.

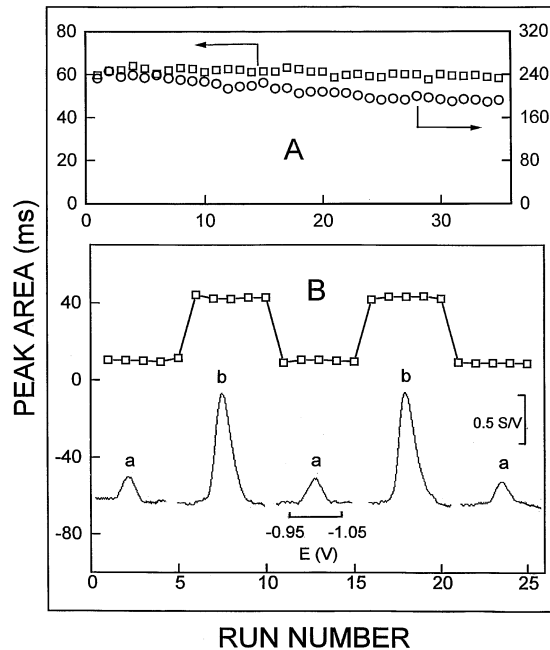


Fig. 4. Repetitive measurements of 25 $\mu\text{g/L}$ nickel (A) and alternative measurements of 5 (a) and 20 $\mu\text{g/L}$ nickel (B). Electrodes were rinsed when transferred from (b) to (a). Accumulation for 10 s at -0.2 V, with a subsequent stripping with a current of -4 μA . Other conditions, as in Figure 1B. \square and \circ represent the iridium and glassy-carbon based mercury electrodes, respectively.

of the constant current upon the nickel response in the presence (a) and absence (b) of oxygen. Using the aerated medium, the peak decreases rapidly with the current between -3.0 and -4.0 μA , then more slowly, and nearly levels off above -6.0 μA . A faster decrease of the nickel signal is observed using the

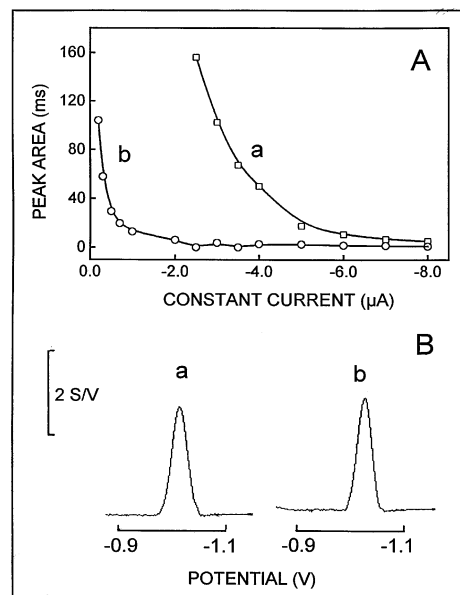


Fig. 5. A) Effect of the constant current upon the response to 20 $\mu\text{g/L}$ nickel at the iridium microarray in the presence (a) and absence (b) of oxygen. B) Typical signals in the presence (a) and absence (b) of oxygen using stripping currents of -3 μA and -0.2 μA , respectively. Accumulation for 10 s at -0.2 V, with a subsequent stripping using a current of -4 μA . Other conditions, as in Figure 1B.

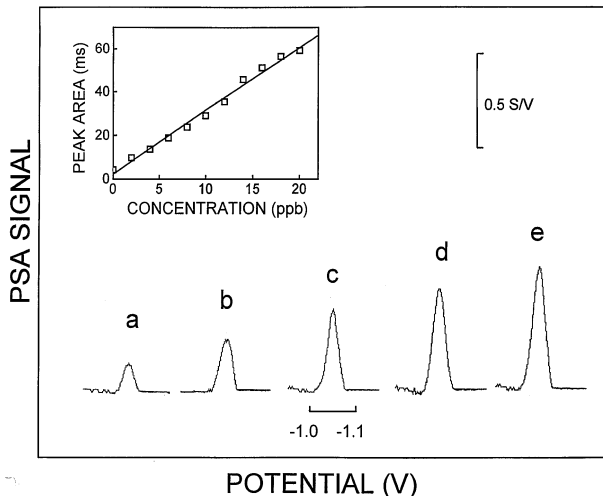


Fig. 6. Potentiograms for successive $2 \mu\text{g/L}$ nickel increments (a–e), along with the resulting calibration plot (inset). Accumulation for 30 s at -0.2 V , with a subsequent stripping with a current of $-4 \mu\text{A}$. Matrix, 5 mL tap water/5 mL ammonia buffer (0.05 M pH 9.2). Other conditions, as in Figure 1B.

nondearated solution between -0.2 and $-1.0 \mu\text{A}$, with a leveling off above $-2.0 \mu\text{A}$. Apparently, part of the applied current is consumed by the dissolved oxygen, leading to different profiles. As indicated from Figure 5B, nearly identical response characteristics are obtained in the presence (a) and absence (b) of oxygen (after a judicious choice of the stripping current), indicating great promise for various on-site and on-line applications.

The well-defined concentration dependence provides the basis for the analytical utility of the iridium-microarray adsorptive stripping sensor. Figure 6 displays potentiograms obtained for increasing the nickel concentration in $2 \mu\text{g/L}$ steps (a–e). Short adsorption times (30 s) are sufficient for obtaining well-defined peaks for these low concentrations. A detection limit of around $0.5 \mu\text{g/L}$ can be estimated based on the signal-to-noise characteristics ($S/N = 3$) of these data. The five peaks shown came from a series of ten successive concentration increments, the results of which are shown as the inset of Figure 6. The response is linear over the entire $2\text{--}20 \mu\text{g/L}$ range tested. The good linearity and low detection limits are coupled with a very good precision (e.g., RSD of 1.7% for 12 repetitive measurements of $50 \mu\text{g/L}$ nickel using 10 s adsorption). Coupling the short accu-

mulation times (10–30 s) used in this study, with the short (1 s) ‘cleaning’ period, such sensitive nickel measurements can be performed at a rate of 60–120 runs per hour.

4. Conclusion

We have demonstrated that iridium-based mercury microelectrode arrays are very suitable for adsorptive stripping measurements of trace nickel. This represents the first application of the iridium-microarray sensor to trace metals that cannot be plated electrolytically. The attractive adsorptive stripping behavior indicates great promise for monitoring other environmentally important contaminants based on the metal-chelate adsorptive approach. Research in these laboratories is progressing towards expanding the scope and applications of iridium-based microelectrode arrays.

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