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Catalytic adsorptive stripping determination of trace chromium (VI) at the bismuth film electrode

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Abstract

A sensitive adsorptive stripping voltammetric protocol at a bismuth-coated glassy-carbon electrode for trace measurements of chromium (VI) in the presence of diethylenetriammine pentaacetic acid (DTPA) is described. The new protocol is based on accumulation of the Cr-DTPA complex at a preplated bismuth film electrode held at −0.80 V, followed by a negatively-going square-wave voltammetric waveform. Factors influencing the stripping performance including the film preparation, solution pH, DTPA and nitrate concentrations, deposition potential and deposition time, have been optimized. The resulting performance compares well with that observed for analogous measurements at mercury film electrodes. A preconcentration time of 7 min results in a detection limit of 0.3 nM Cr(VI) and after 2 min a relative standard deviation at 20 nM of 5.1% ($n = 25$). Applicability to river water samples is demonstrated. The attractive behavior of the new "mercury-free" chromium sensor holds great promise for on-site environmental and industrial monitoring of chromium (VI). Preliminary data in this direction using bismuth-coated screen-printed electrodes are encouraging.

Keywords: Bismuth film electrode; Chromium (VI); Diethylenetriammine pentaacetic acid (DTPA); Adsorptive stripping voltammetry; Square wave voltammetry

1. Introduction

Considerable interest has developed in the determination of trace chromium (VI) in environmental and industrial sites. Electroanalytical techniques have frequently been used for the determination of chromium (VI) in various matrices. In particular, adsorptive stripping voltammetry offers a highly sensitive detection of chromium in connection to low-cost portable instrumentation [1–3]. For this purpose the adsorptive collection of complexes of chromium with diethylenetriammine pentaacetic acid (DTPA) [1,2] or cupferron [3] is followed by voltammetric measurements of the adsorbed complex. Two basic electrode systems, the mercury-film electrode (MFE) and hanging mercury drop electrode (HMDE), are generally used for adsorptive stripping voltammetric measurements of chromium (VI). Yet, because of the toxicity of mercury, new alternative electrode materials—with a similar performance—are highly desired, particularly for meeting the growing demands for on-site environmental monitoring of trace chromium.

This paper describes a highly sensitive adsorptive stripping procedure for determining trace chromium at a bismuth film electrode. Bismuth-film electrodes, have been shown extremely useful alternatives to mercury electrodes for anodic stripping voltammetric measurements of trace metals [4]. Bismuth is an environmentally-friendly element, with very low toxicity, and a widespread pharmaceutical use. Most recent stripping work at bismuth film electrodes has been devoted to the detection of electrolytically deposited heavy metals including lead, cadmium or zinc [4–6]. The applicability of bismuth electrodes for adsorptive stripping studies has been limited to trace measurements of trace nickel and cobalt in the presence of dimethylglyoxime [7,8]. In the following sections we investigate and demonstrate an attractive adsorptive-stripping protocol for the determination of Cr(VI) via its reduction and subsequent complexation with DTPA at a bismuth film electrode.

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2. Experimental

2.1. Apparatus and reagents

Square wave stripping voltammetric measurements were conducted using an Electrochemical Analyzer 621A (CH Instruments, Austin, TX) connected to a Pentium 2240X computer. The cell assembly consisted of a bismuth-coated glassy carbon (GC, 3 mm diameter, CH Instruments, Austin, TX) working, Ag/AgCl reference (Model CHI111, CH Instruments), and platinum wire counter electrodes. These electrodes were inserted into the 15 mL electrochemical cell (BAS, Model VC-2). Some experiments employed a screen-printed carbon working electrode. pH measurements were performed with a pH meter AB-15 (Accumet Basic, Fisher Scientific). All glassware were soaked in 1 M nitric acid and were rinsed several times with deionized water prior to use.

A semi-automatic screen printer (Model TF 100; MPM, Franklin, MA) was used for printing the carbon thick film electrodes. The carbon ink (Acheson) was printed through a patterned stencil on 10 cm × 10 cm ceramic plates containing 30 strips (3.3 cm × 1.0 cm each). The resulting printed carbon thick film electrodes were cured for 1 h at 200 °C. An insulating ink (Ercon) was subsequently printed on a portion of the plate, leaving 4 mm × 2 mm sections on both ends giving a defined working electrode area and an electrical contact. The insulating layer was cured at 150 °C for 2 h.

Sodium acetate, 1000 μg mL^{-1} stock solutions of chromium (VI), bismuth, and mercury were purchased from Aldrich. The DTPA (Aldrich) solution (0.1 M) was prepared by dissolving an appropriate amount of the ligand and adding of 25% ammonium hydroxide till pH 6.0. Potassium nitrate (Fisher Scientific) was prepared by dissolving a corresponding amount of the salt in deionized water. The river water sample, collected from the Rio Grande River in Las Cruces (NM), was used without any pre-treatment.

2.2. Deposition of the bismuth or mercury film

The bismuth or mercury-coated electrodes were prepared by 120 s deposition at −1.20 V from a 0.1 M acetate buffer (pH 4.5) solution containing either 500 μg L^{-1} bismuth or 10 mg L^{-1} mercury, respectively.

2.3. Adsorptive stripping measurements of Cr(VI)

The supporting electrolyte contained 0.1 M acetic buffer (pH 6.0) and 0.25 M potassium nitrate. After deareating with pure nitrogen for 5 min, DTPA was added to a final concentration of 5 mM. This was followed by a 2 min adsorptive accumulation at −0.8 V under magnetic stirring. The electrode was then held for 5 s at −0.80 V in the unstirred sample before the square wave voltammogram (SWV) was recorded (using a step potential of 5 mV, amplitude of 25 mV and frequency of 20 Hz) over the −0.80 to −1.40 V range. Between successive measurements, a pre-cleaning step was applied with a potential at −1.20 V for 10 s. All adsorptive stripping voltammograms have been baseline corrected by subtraction of the background signal. The baseline curve was fitted (to a six order polynomial equation) and then subtracted from the original SWV plot.

3. Results and discussion

Combining the bismuth film electrode with the DTPA-based adsorptive stripping procedure results in a well-defined response, with high sensitivity and good reproducibility. Fig. 1 compares the adsorptive stripping voltammetric response for 20 nM Cr(VI) obtained at the mercury (A) and bismuth (B) coated glassy carbon electrodes. Both electrodes display a well defined, reductive peak at −1.22 V (Hg) and −1.10 V (Bi), corresponding to the one-electron reduction and removal of the adsorbed Cr(III) complex from the electrode surface. Examination of the stripping signal reveals that the bismuth film not only lowers the reduction potential of the Cr(III) complex, but also enhances the stripping response compared to the mercury electrode (note the different scales). Overall, the data of Fig. 1 indicate that the stripping performance is not compromised by the use of the bismuth film (instead of the mercury coating).

3.1. Effect of the bismuth film on the analytical signal

Initial optimization of the analytical signal centered upon varying the thickness of the bismuth film. This was carried out by keeping both the film deposition time (120 s) and potential (−1.20 V) constant while changing the concentration of bismuth ion in the plating solution. Fig. 2 shows the influence of the bismuth concentration upon the adsorptive stripping signal for 20 nM chromium. The response increases rapidly with the level of bismuth at first up to 0.2 mg L^{-1} then more slowly, and nearly levels off above 0.4 mg L^{-1}

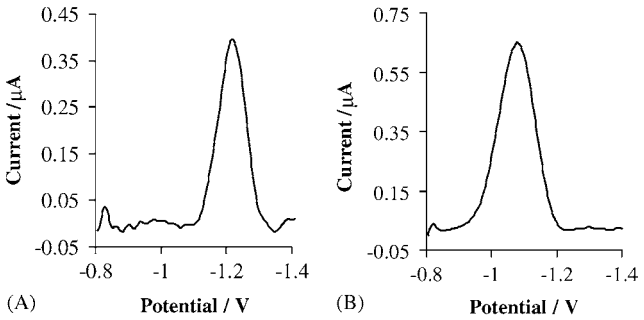

Fig. 1. Stripping voltammograms of 20 nM Cr(VI) at mercury (A) and bismuth (B) coated glassy carbon electrodes. Accumulation for 120 s at −1.0 V with mercury film and −0.8 V with bismuth film. Solution: 0.1 M acetate buffer (pH 6.0) containing 10 mM DTPA and 0.25 M KNO_3. SWV detection conditions: step potential, 5 mV; amplitude, 25 mV; frequency, 20 Hz, along with background correction.

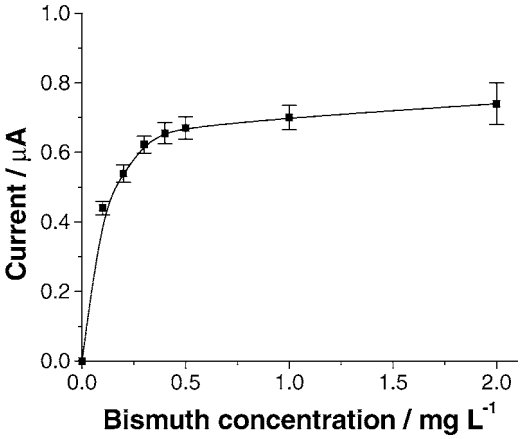

Fig. 2. Effect of the bismuth concentration upon the stripping voltammetric response of 20 nM Cr(VI). Two-minute accumulation at −0.8 V; DTPA concentration, 10 mM. Other conditions, as in Fig. 1B.

bismuth. Such profile reflects the coverage of the glassy-carbon substrate. It was further noted that when the bismuth concentration was higher than 2.0 mg L^{-1} the film became unstable upon transferring to the sample solution. All subsequent experiments were conducted using a bismuth-film electrode formed in a plating solution containing 0.5 mg L^{-1} bismuth, in connection to 2 min deposition at −1.20 V and a square-wave voltammetric scan. Square wave voltammetry was used due to its speed advantage and previous success for the determination of Cr(VI) at mercury electrodes [9].

3.2. Optimization of the analytical signal

Further examination of the detection process focused on studying the effect of solution conditions, such as pH and concentration of DTPA, upon the stripping response to Cr(VI). Fig. 3A depicts the variation in the stripping current peak of 20 nM Cr(VI) as a function of pH. The response increases rapidly with the pH between 4.5 and 6.0, and decreases rapidly at higher pH values. These results are consistent with those reported previously for the determination of Cr(VI) using the DTPA complexing agent at mercury electrodes [2]. Based on the pKa of the DTPA species the predominant species at pH 6 are H_2Y^{3-} and H_3Y^{2-} (with the latter yielding the most stable complex with Cr(III) [10]). The peak potential was found to be independent of pH thereby confirming that no protons are exchanged in the reduction process.

Further characterization of the analysis medium focused on investigating the effect of the DTPA concentration upon the analytical signal. This was conducted by measuring the peak current obtained in a 5 nM chromium solution containing different DTPA concentrations (Fig. 3B). These results show a sharp increase in the stripping signal upon increasing the DTPA concentration from 0 to 5 mM. The peak current was found to be independent of the ligand concentration when it was increased further (>5 mM). Further studies were conducted utilizing a DTPA concentration of 5 mM.

Final characterization of the analysis medium examined the effect of the oxidant (NO_3^-) concentration upon the analytical signal. This was carried out by recording the peak current for 20 nM Cr(VI) in the presence of different concentrations of KNO_3. The corresponding plot of the measured peak current against concentration of KNO_3 is detailed in Fig. 3C. This shows a rapid increase up to 0.25 M KNO_3 and a slower one thereafter. Subsequent experiments were conducted using a KNO_3 concentration of 0.25 M.

We next turned our attention to investigate the effects of varying the electrochemical accumulation parameters (time and potential) on the stripping signal. Fig. 4A displays the influence of the accumulation potential on the Cr-DTPA peak current. The chromium peak increases slowly with the potential between −0.40 and −0.60 V, then more rapidly, reaching its maximum value at −0.80 V. A sharp lowering in the analytical signal is observed at more negative potentials. This profile reflects the influence of the electrode potential upon two processes, namely the reduction of Cr(VI) to Cr(III) and the adsorptive accumulation of the Cr(III)–DTPA complex. At potentials more negative than −0.80 V Cr(III) is expected to be further reduced to Cr(II), lowering the availability of Cr(III) essential for the complexation [11]. All further measurements were carried out with a deposition potential of −0.80 V.

The influence of the accumulation time upon the analytical signal was subsequently examined. Fig. 4B depicts the

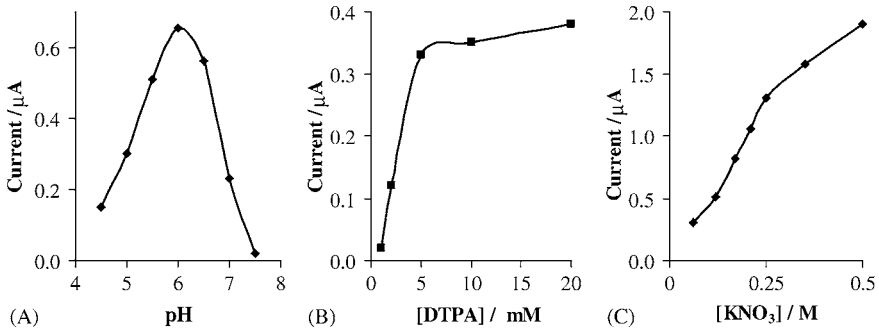

Fig. 3. Effect of the pH (A), DTPA concentration (B) and KNO_3 concentration (C) upon the response to 20 nM (A and C) and 5 nM (B) Cr(VI). DTPA level 10 mM (A), 5 mM (C), KNO_3 level, 0.25 M (A and B). Other conditions, as in Fig. 1B.

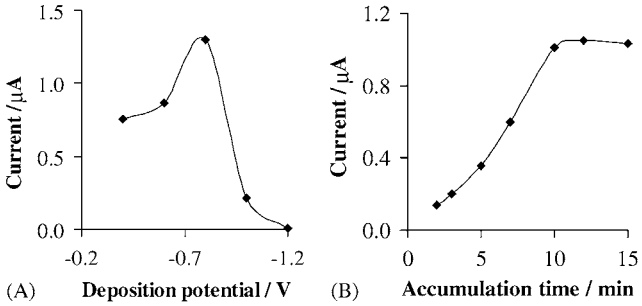

Fig. 4. Effect of the accumulation potential (A) and time (B) upon the response to 20 nM and 1 nM Cr(VI), respectively. DTPA concentration, 5 mM. accumulation time, 2 min (A); accumulation potential, −0.8 V (B). Other conditions, as in Fig. 1B.

variation in the peak current with the accumulation time for 1 nM Cr(VI). The response increases nearly linearly with the accumulation time up to 10 min accumulation, and levels off thereafter. Analogous behavior was observed for the determination of 20 nM Cr(VI) (data not shown). However, in the latter case the leveling off occurred at ca. 5 min, reflecting the faster surface saturation. An accumulation time of 2 min was utilized for all further measurements.

3.3. Analytical characterization

The bismuth-coated electrode offers a well-defined concentration dependence. Fig. 5A displays stripping voltammograms recorded for increasing Cr(VI) concentration, over the 5–50 nM range (a–h). Well defined peaks are observed following a 2-min adsorptive accumulation. The peak current increases proportionally with the metal concentration to yield a highly linear calibration plot (B), with a slope of 0.07 μA nM^{-1} (correlation coefficient, 0.996). Even lower concentrations can be detected in connection to longer adsorption periods. For example, a detection limit of ca. 0.3 nM was estimated on the basis of the signal-to-noise characteristics ($S/N = 3$) of the response for a 1.0 nM Cr(VI) solution following a 7 min accumulation (Fig. 5C). These results compare favorably with those obtained for similar protocols at mercury film electrodes [12,13].

The sensitive response of the bismuth electrode is also highly reproducible. A series of 25 successive measurements for 20 nM chromium yielded a mean peak current of 1.32 μA, a range of 1.15–1.45 μA and a relative standard deviation (R.S.D.) of 5.1%. (conditions, as in Fig. 1B). Such a stable response, over a prolonged continuous 1 h operation reflects the high stability of the preplated bismuth film. Possible interferences from co-existing trace metals (present at five-fold excess) were investigated. The following metals were tested at the 25 nM level and found not to affect the response for 5 nM chromium (VI): Pb(II), Cd(II), Zn(II), Cu(II), Fe(III), Ni(II), and Co(II). A large (20-fold) excess of hydrated Cr(III) did not affect the response of 5 nM Cr(VI). This is consistent with previous studies which have shown the effective discrimination against hydrated Cr(III) species [2].

The new electrochemical detection is suitable for measuring chromium (VI) in natural water systems. Fig. 6 demonstrates the suitability of the system for monitoring low levels of chromium in an untreated river water sample. Well defined peaks ($E_p = -1.16$ V; $b_{1/2} = 170$ mV) are observed for increasing Cr(VI) concentrations in 5 nM steps (a–e). The peak height increases linearly with the Cr(VI) concentration over the entire range examined (0–25 nM). The experiment was repeated three times in order to assess the reproducibility of the stripping protocol in real media. The resulting calibration plots produced a mean sensitivity of 0.091 ± 0.008 μA nM^{-1} ($n = 3$). Note that the sensitivity observed for the real sample is similar to that (0.07 μA nM^{-1}) reported above for synthetic samples, indicating minimal matrix effects. The low percentage error (8.8%) in the sensitivity data thereby demonstrates the robustness of the discussed protocol. The flat response of the unspiked sample (dotted line) indicates the absence of potential interferences.

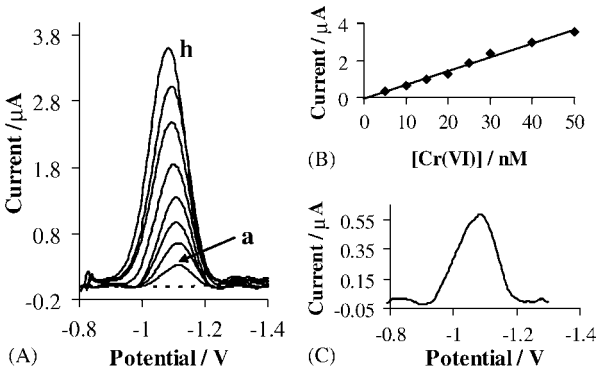

Fig. 5. (A) Adsorptive stripping curves of Cr(VI) concentrations from 0 to 50 nM (in 5 nM (a–f) and 10 nM (g and h) steps); (B) the corresponding calibration plot. (C) Response to 1 nM Cr(VI). DTPA concentration, 5 mM; accumulation potential, −0.8 V; accumulation time 2 min (A) and 7 min (C). Other conditions, as in Fig. 1B.

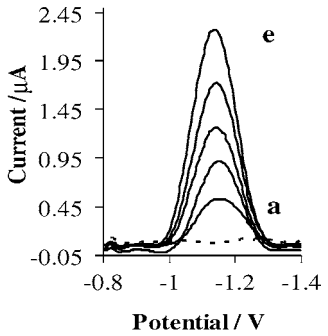

Fig. 6. Adsorptive stripping voltammograms for a river water sample spiked with 5, 10, 15, 20 and 25 nM Cr(VI) (a–e). Conditions, as in Fig. 5A.

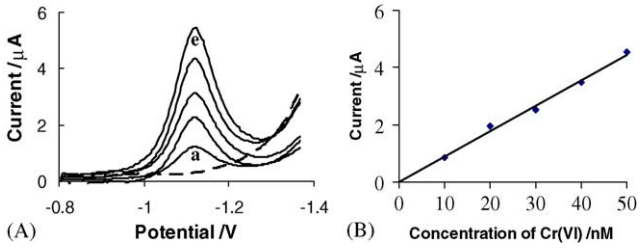

Fig. 7. (A) Adsorptive stripping curves of Cr(VI) concentrations from 0 to 50 nM (in 10 nM (a–e) steps) obtained at a bismuth coated SPE; (B) the corresponding calibration plot. Other conditions, as in Fig. 1B.

3.4. Towards a disposable sensor

In order to facilitate field measurements of trace chromium it would be desirable to replace the glassy carbon substrate with a disposable screen-printed electrode (SPE). Fig. 7A displays stripping voltammograms recorded for increasing Cr(VI) concentrations over the 10–50 nM range (a–h) at a bismuth-coated SPE. Well defined peaks are observed following a 2 min adsorptive accumulation. The peak current increases proportionally with the metal concentration to yield a highly linear calibration plot (B), with a slope of 0.089 μA nM^{-1} (correlation coefficient, 0.995). The similar sensitivities obtained at both the GC and SPE bismuth film electrodes are consistent with the two electrodes having approximately the same surface area. The precision of the voltammetric signal was examined using 10 repetitive measurements of a 20 nM Cr(VI) solution. These data produced an average peak current of 1.98 μA and a relative standard deviation of 9.8%.

4. Conclusions

The above results demonstrate the suitability of bismuth film electrodes for adsorptive stripping voltammetric measurements of trace Cr(VI). The protocol has been optimized in depth by examining the influence of the bismuth film, the detection solution pH, DTPA concentration, accumulation time and potential. The resulting adsorptive stripping performance is not compromised by the use of a "mercury-free" surface. Coupling this favorable performance with the negligible toxicity of bismuth, makes the bismuth-coated electrodes extremely attractive for on-site environmental and industrial measurements of Cr(VI), and for addressing possible restrictions on the use of mercury electrode materials.

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