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Catalytic adsorptive stripping voltammetric measurements of trace vanadium at bismuth film electrodes

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Abstract

Bismuth-coated glassy carbon electrodes have been successfully applied for catalytic adsorptive stripping voltammetric measurements of low levels of vanadium(V) in the presence of chloranilic acid (CAA) and bromate ion. The new protocol is based on the accumulation of the vanadium-chloranilic acid complex from an acetate buffer (pH 5.5) solution at a preplated bismuth film electrode held at −0.35 V (versus Ag/AgCl), followed by a square-wave voltammetric scan. Factors influencing the adsorptive stripping performance, including the CAA and bromate concentrations, solution pH, and accumulation potential or time have been optimized. The response compares favorably with that observed at mercury film electrodes. A linear response is observed over the 5–25 μg/L concentration range (2 min accumulation), along with a detection limit of 0.20 μg/L vanadium (10 min accumulation). High stability is indicated from the reproducible response of a 50 μg/L vanadium solution (*n* = 25; R.S.D. = 3.1%). Applicability to a groundwater sample is illustrated.

Keywords: Vanadium; Bismuth film electrode; Chloranilic acid (CAA); Catalytic adsorptive stripping voltammetry

1. Introduction

Vanadium is widely used and released in various industrial process [1]. While this metal represents an essential element at trace amounts, it is toxic when presents at higher concentrations. Owing to the low levels of vanadium in natural samples, highly sensitive methods are required for its determination. Few techniques, such as neutron activation, graphite-furnace atomic absorption spectroscopy, ICP-MS and stripping voltammetry, can meet the challenge of trace vanadium measurements in environmental samples. Among those, only the electrochemical method can be readily adapted for on-site (field) measurements of trace vanadium. In particular, adsorptive stripping voltammetry (AdSV), based on the interfacial accumulation and voltammetric determination of metal complexes, has been shown useful for determining vanadium in various matrices [2–7]. Different complexing agents, such as catechol [2], cupferron [3,4], Solchrome Violet RS [5] or chloranilic acid [6,7], have been proposed. Several of these protocols involve a catalytic enhancement of the response in the presence of the bromate oxidant [3,7]. A limitation of these AdSV protocols, particularly for on-site monitoring of vanadium, is their reliance on a stationary (hanging) mercury drop working electrode. Reliable 'non-mercury' vanadium AdSV sensors, not compromising the attractive performance of mercury electrodes, should particularly benefit field measurements of vanadium.

This aim of this work was to optimize and characterize an effective catalytic adsorptive stripping protocol for trace measurements of vanadium(V) at a bismuth film electrode (BFE), based on the adsorptive accumulation and reduction of the chloranilic acid/V complex in the presence of bromate. Chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) (CAA) forms electroactive adsorbable complexes selectively with vanadium and few other metals [6–8]. Bobrowski et al. [7] reported recently on the highly sensitive catalytic adsorptive measurements of the V-CAA-bromate system at a hanging mercury drop electrode. Bismuth electrodes have attracted considerable attention as an attractive alternative to mercury electrodes used in stripping analysis [9,10]. Most early stripping applications of BFEs focused on measurements of elec-

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trodeposited heavy metals. The suitability of BFEs for AdSV has been demonstrated recently in connection to trace measurements of nickel [11], cobalt [12], uranium [13], or chromium [14]. As will be illustrated below, the adsorptive accumulation of V-CAA complexes onto the BFE results in a highly sensitive, selective and reproducible AdSV protocol for measuring trace levels of vanadium.

2. Experimental

2.1. Apparatus and reagents

Catalytic adsorptive stripping voltammetric measurements were conducted using Autolab PGSTAT 10 electrochemical analyzer (ECO, Chemie BV, Utrecht, Netherlands) connected to personal computer. Bismuth-coated glassy carbon disk (3 mm diameter, CH Instruments, Austin, TX), Ag/AgCl (model CHI111, CH Instruments), and platinum wire served as the working, reference and counter electrodes, respectively. These electrodes were inserted into the 15 mL electrochemical cell (BAS, model VC-2). All glassware was soaked in 1 M nitric acid and was rinsed several times with deionized water prior to use.

Sodium acetate and stock solutions of vanadium, bismuth, and mercury (1000 μg/mL) were purchased from Aldrich. The CAA (Aldrich) solution (0.1 M) was prepared by dissolving an appropriate amount of the ligand in deionized water. Potassium bromate (Aldrich) was prepared by dissolving a corresponding amount of the salt in deionized water. The groundwater sample, collected in Scottsdale (AZ) was used without any pretreatment, with the exception of adding a 10% volume of the acetate buffer (pH 5.5) electrolyte.

2.2. Procedure

The bismuth or mercury-coated electrodes were prepared by a 600 s electrodeposition at −1.0 V from a 0.1 M acetate buffer (pH 4.5) solution containing either 100 μg/L bismuth or mercury ions. The electrode was then washed and transferred rapidly to the sample solution.

All measurements were conducted at room temperature using nondearated samples. The supporting electrolyte solution contained 0.1 M acetate buffer (pH 5.5), 50 μM CAA and 4 mM potassium bromate. The adsorptive accumulation step proceeded for 2 min at −0.35 V under magnetic stirring. Stirring was then stopped and after 15 s the square wave voltammogram (SWV) was recorded (using a step potential of 4 mV, amplitude of 25 mV and frequency of 25 Hz) over the −0.35 to −1.20 V range. A ‘cleaning step’ (15 s at −1.20 V) was employed between successive measurements.

3. Results and discussion

3.1. Optimization of the analytical protocol

Combining the bismuth film electrode with the CAA-based adsorptive stripping procedure resulted in a well-defined and reproducible response for trace vanadium(V). Fig. 1 compares the adsorptive stripping voltammetric response for 20 μg/L vanadium, obtained at the mercury (A) and bismuth (B) coated glassy carbon electrodes. Both electrodes display a well-defined reduction peak at −0.58 V (Hg) and −0.63 V (Bi) corresponding to the one-electron V(V) to V(IV) reduction and removal of the adsorbed V complex from the electrode surface. Examination of the stripping signals reveals that the signal-to-background characteristics are not compromised by the use of the bismuth film (instead of the mercury coating). As indicated from the different current scales, the BFE displays a substantially larger stripping response. The removal of the V-CAA complex from the surface was indicated from repetitive cyclic voltammetric measurements of the accumulated complex over the −0.35 to −1.20 V range. These displayed a single well-defined reduction peak (at −0.66 V) during the first scan, and no peaks in the reverse scan or in the subsequent scans (not shown).

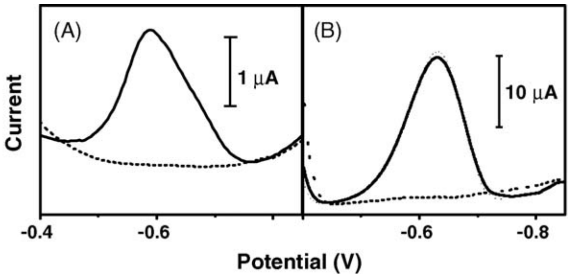

Fig. 1. Square-wave adsorptive stripping voltammograms for 20 μg/L vanadium along with the background response (dotted line) in the presence of 50 μM chloranilic acid and 4 mM bromate at mercury (A) and bismuth (B) coated glassy carbon electrodes. Supporting electrolyte, 0.1 M acetate buffer (pH 5.5); accumulation, −0.35 V for 120 s with stirring, followed by a square-wave potential scanning with a step potential of 4 mV, an amplitude of 25 mV, and a frequency of 25 Hz.

The effect of the pH on the stripping response was evaluated over the 3.0–6.5 range. The response for 20 μg/L V(V) increases slowly between 3 and 4, followed by a sharp rise between pH 4.0 and 5.5; a sharp decrease of the vanadium peak is observed at higher pH values. The V-CAA peak potential shifted from −0.38 to −0.66 V upon increasing the pH between 4.0 and 6.5. All subsequent work involved a pH 5.5 solution. A quite similar optimal pH of 4.8 was reported recently for analogous measurements at the hanging mercury drop electrode [7]. Such profile reflects the pH effect upon the multiple processes involved in the assay, including the V-CAA complexation, the interfacial (adsorption) and catalytic steps, and the reduction of the adsorbed complex.

The influence of the ligand and oxidant concentrations upon the vanadium signal was also examined using a 20 μg/L vanadium solution. The response increases in a nearly linear fashion up to 30 μM CAA and 3.5 mM bromate and starts to level off thereafter (Fig. 2B and C, respectively). Clearly, the addition of bromate ion leads to a substantial (4-fold) enhancement of the reduction peak of the complex due to the catalytic reaction between the reduced complex and the BrO_3^- ion. Subsequent analytical work was performed using CAA and $KBrO_3$ concentrations of 50 μM and 4 mM, respectively, and in the presence of dissolved oxygen.

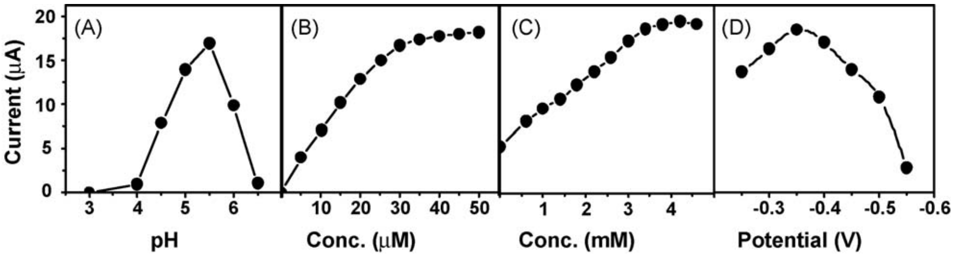

Fig. 2. Effect of the solution pH (A), chloranilic acid concentration (B), bromate concentration (C) and of the accumulation potential (D) upon the catalytic adsorptive stripping response of 20 μg/L vanadium at the BFE. Other conditions, as in Fig. 1B.

Next we turned our attention to investigate the effect of the accumulation conditions on the vanadium signal. Fig. 2D displays the influence of the accumulation potential on the V-CAA peak current. Potentials lower than −0.25 V could not be used due to the oxidation of the bismuth film. The peak rises slowly between −0.25 and −0.35 V and decreases gradually thereafter. An accumulation potential of −0.35 V was used for further measurements. The influence of the accumulation time is displayed in Fig. 3. The response increases linearly with accumulation time up to 1 min, then more slowly up to 3 min, and levels off at longer periods. See inset A for the corresponding current–time dependent plot. We also compared different stripping modes, including linear scan voltammetry, differential pulse voltammetry and square-wave voltammetry and found that the latter offered the most favorable response characteristics and speed (not shown). All analytical work was performed using the square-wave stripping mode.

3.2. Analytical characterization

The adsorption and stripping processes of the V-CAA complex at the bismuth film electrode are highly reproducible. Fig. 3B displays stripping voltammograms recorded during a prolonged series of 25 repetitive measurements of 50 μg/L vanadium. A highly stable response, with a mean peak current of 21.85 μA, and a relative standard deviation (R.S.D.) of 3.1%, is observed over this 70 min operation. Such behavior indicates an effective removal of the V-BAA complex from the BFE surface during the scan and the subsequent 15 s ‘cleaning’ step. The absence of memory effects offers great promise for continuous monitoring applications.

The bismuth-coated electrode offers a well-defined concentration dependence. Fig. 4 shows stripping voltammograms for increasing concentrations of vanadium(V) over the 5–40 μg/L range (a–h). Well-defined peaks are observed following a 2 min accumulation. As expected for such adsorptive preconcentration, the peak current increases proportionally with the vanadium concentration up to 25 μg/L and more slowly at higher concentrations. The corresponding calibration plot (shown in inset A) has an initial (5–25 μg/L) linear portion with a slope of 1.0 μA L/μg and correlation coefficient of 0.997. Lower concentrations can be readily detected in connection to longer adsorption periods. For example, a detection limit of ca. 0.20 μg/L was estimated on the basis of the signal-to-noise characteristics ($S/N = 3$) of the response for a 1.0 μg/L V solution following a 10 min accumulation (Fig. 4B). Note that this detection limit is higher than those (0.25–10 ng/L) reported at mercury drop electrodes [2–7].

The CAA-based BFE catalytic adsorptive voltammetric procedure leads to a selective vanadium(V) response. Possible interferences from co-existing trace metals (present at a 20-fold excess) were investigated. The following metals were thus tested at the 1 mg/L level and found not to affect the response for

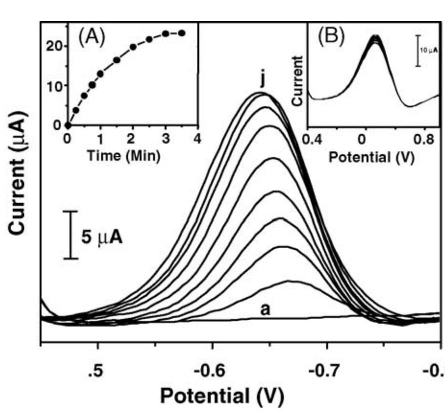

Fig. 3. Effect of accumulation time: AdSV response of 20 μg/L vanadium following accumulation for 0, 15, 30, 45, 60, 90, 120, 150, 180 and 210 s (curves a–j) at −0.35 V. Also shown, (inset A) is the resulting current-time plot and (inset B) 25 successive voltammograms for a 50 μg/L vanadium solution recorded during a 70 min period. Other conditions, as in Fig. 1B.

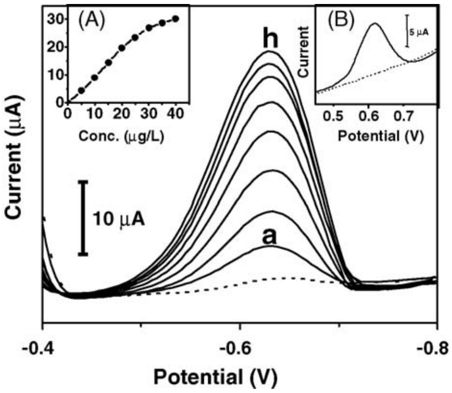

Fig. 4. Square-wave adsorptive stripping voltammograms for increasing levels of vanadium in 5 μg/L steps (curves a–h), along with the background response (dotted line). Accumulation potential and time, −0.35 V and 120 s, respectively. Also shown (inset A) is the resulting calibration plot and (inset B) is a voltammogram for a 1 μg/L vanadium solution following a 10 min accumulation, along with the background response (dotted line). Other conditions, as in Fig. 1B.

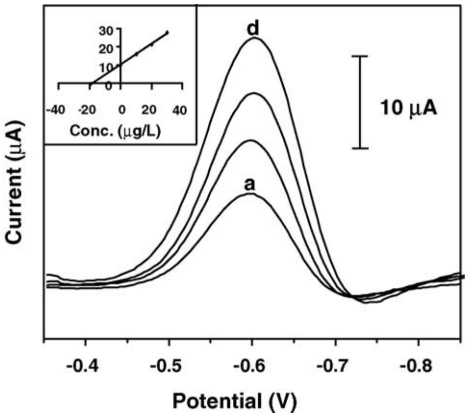

Fig. 5. Adsorptive stripping voltammograms for a groundwater sample [9:1 sample/acetate buffer (pH 5.5)] (a) and three successive standard additions of vanadium in 10 μg/L steps (b–d). Also shown (inset) is the resulting standard addition plot. Other conditions, as in Fig. 1B.

50 μg/L vanadium: Ag(I), Al(III), Au(I), Be(II), Cd(II), Cr(III), Cu(II), Fe(III), Hg(II), Mo(VI), Ni(II), Pb(II), Pt(II), Sb(III), Ti(II), U(VI) and Zn(II). New peaks (at −0.88 and −1.02 V) were observed in the presence of Mo(VI) and V(VI), respectively. These peaks had no affect upon the V-CAA signal. Similar Mo and U signals were reported in the presence of CAA at mercury drop electrodes [8]. Somewhat surprising is the absence of Sb(III) interference, in view of the Sb effect on the V-CAA response at the mercury drop electrode [7].

The high selectivity of the V-CAA BFE procedure enables direct measurements in relevant environmental samples. For example, Fig. 5 demonstrates the suitability of the new BFE-based protocol for measuring vanadium in natural waters. This figure shows adsorptive stripping voltammograms for an untreated groundwater sample (a), and following spiking it with increasing concentrations of vanadium in 10 μg/L steps (b–d). The sample contained moderately high hardness and alkalinity (pH ~8.2) and moderately high total dissolved solids (~1000 mg/L). A vanadium level of 20 μg/L can be estimated for the original sample, based on the resulting standard additions plot (shown as inset). Such value is in agreement with that (23 μg/L) estimated from analogous atomic absorption spectroscopic measurements. The well-defined peak and background profiles indicate negligible matrix effects.

4. Conclusions

The CAA-bromate system has been found to be very suitable for catalytic-AdSV measurements of trace vanadium at BFEs. The new protocol has been optimized by examining the influence of the detection solution (pH, CAA and bromate concentrations) and accumulation conditions. The study further expands the scope of BFEs and represents an additional step towards the replacement of mercury electrodes in adsorptive stripping voltammetry. The attractive behavior of the CAA complex of vanadium indicates great promise for field monitoring of trace vanadium, for developing additional AdSV protocols of other metal-CAA complexes (e.g., Sb, Mo, U) [15], as well for the simultaneous measurements of these metals (along with V), in a manner similar to that reported for mercury drop electrodes. These directions, along with fundamental studies onto the interfacial activity of metal-CAA complexes at BFEs, are currently being examined.

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