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Trace vanadium analysis by catalytic adsorptive stripping voltammetry using mercury-coated micro-wire and polystyrene-coated bismuth film electrodes

Royce Dansby-Sparks, James Q. Chambers, and Zi-Ling Xue

Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996, USA

Abstract

An electrochemical technique has been developed for ultra trace (ngL^{-1}) vanadium (V) measurement. Catalytic adsorptive stripping voltammetry for V analysis was developed at mercury-coated gold micro-wire (MWE, 100 μm) electrodes in the presence of gallic acid (GA) and bromate ion. A potential of -0.275 V (vs Ag/AgCl) was used to accumulate the complex in acetate buffer (pH 5.0) at the electrode surface followed by a differential pulse voltammetric scan. Parameters affecting the electrochemical response, including pH, concentration of GA and bromate, deposition potential and time have been optimized. Linear response was obtained in the $0\text{--}1000\text{ ngL}^{-1}$ range (2 min deposition), with a detection limit of 0.88 ngL^{-1} . The method was validated by comparison of results for an unknown solution of V by atomic absorption measurement. The protocol was evaluated in a real sample by measuring the amount of V in river water samples. Thick bismuth film electrodes with protective polystyrene films have also been made and evaluated as a mercury free alternative. However, ngL^{-1} level detection was only attainable with extended (10 min) deposition times. The proposed use of MWEs for the detection of V is sensitive enough for future use to test V concentration in biological fluids treated by the advanced oxidation process (AOP).

Keywords

vanadium; gallic acid; catalytic adsorptive stripping voltammetry; micro-wire electrode

Introduction

Vanadium is the 21st most abundant element in the earth's crust [1], and it is released in large quantities into the environment by the burning of fossil fuels and industrial processes [2]. Vanadium concentrations in natural waters can range from 10 to 40 nM [3] and are a good indicator of urban pollution levels [4]. It is an element of considerable environmental interest because of its wide use in a variety of industrial applications and because of its narrow thresholds between essential and toxic levels in living organisms [5]. Due to the low concentrations present in these samples, highly sensitive and field portable methods of analysis are desirable.

The impact of vanadium on human health has also been noted. Vanadium is thought to be an essential trace element but toxic at elevated levels. The use of vanadium supplements to treat

diabetes remains controversial as its efficacy has not been definitely proven in humans [1]. The supplements provide various insulin-like effects in *in-vitro* and *in-vivo* systems, and have shown the ability to improve glucose homeostasis (metabolic equilibrium) and insulin resistance in Type 1 and Type 2 diabetes [1,2,6–8]. An understanding of the efficacy and monitoring of the safety of vanadium for long-term use is desired. The levels of vanadium in human blood and urine have been reported to be ca. 50 and 510 ngL⁻¹, respectively [2]. The analysis of blood and urine samples often requires pretreatment which tends to increase their volumes [9]. Therefore, a sensitive method, at the low ngL⁻¹ level, is needed for the detection of V in biological fluids.

Reliable measures for assessing V status in humans and environmental samples are very limited. Three analytical techniques, neutron activation, inductively coupled plasma mass spectrometry [(ICP-MS) such as (high resolution) HR-ICP-MS or (dynamic reaction cell) DRC-ICP-MS], and graphite furnace atomic absorption spectroscopy (GF-AAS), have the required sensitivity for V measurement in biological samples from humans and low-level environmental samples [10]. However, these techniques are very specialized, bulky, and expensive, making their use for routine analysis difficult.

Sensitive electrochemical techniques have been developed for trace V analysis. Electrochemical methods are far less expensive and are more portable than the three aforementioned techniques. Specifically, catalytic adsorptive stripping voltammetry (CAAdSV) has proven useful for trace V detection. These techniques use complexing ligands such as chloroanilic acid [10,11], cupferron [12], catechol [3], or gallic acid [13] to absorb the target metal ions on the surface of the electrode. The electrode reduces the absorbed complex, after which a chemical oxidant re-oxidizes the complex making it available for direct electrode reduction many times during the scan. This cyclic reaction in combination with the preconcentration of the complex on the electrode surface increases the faradaic current response and results in a highly sensitive technique [14]. Traditionally, mercury-based electrodes have been used with sub- ngL⁻¹ detection limits [11,12]. More recently, Wang and coworkers have demonstrated the use of non-toxic bismuth film electrodes as an alternative to mercury based electrodes [10]. However, the limit of detection of bismuth film electrodes was three orders of magnitude higher than those of mercury-based electrodes. Therefore, an alternative to mercury-drop and film electrodes that maintains the required sensitivity for ultra trace vanadium detection is highly desired.

In the current work, the development of an aqueous V(V) analysis by CAAdSV using gallic acid as the ligand is described. Mercury-coated gold microwire electrodes (MWEs) are demonstrated for use in CAAdSV detection of V for the first time with a detection limit of 0.88 ngL⁻¹. The electroanalytical protocol is optimized and characterized for an effective CAAdSV technique for V analysis. MWEs are used for the detection of V in untreated river water by the standard addition method and the method is validated by quantification of a V standard of unknown concentration. In addition, our work to develop a mercury free polystyrene-coated bismuth film electrode is described.

Experimental

Apparatus and reagents

Electrochemical measurements were conducted using Electrochemical Workstation 650A/440A (CH Instruments, Austin, TX) connected to a computer. The working electrode was either a mercury-coated gold micro-wire working electrode or a bismuth modified glassy carbon electrode (3 mm diameter, Cypress Systems, 66-EE047) described below. Ag/AgCl (model CHI111, CH Instruments) and platinum wire were used as reference and counter electrodes, respectively. The electrodes were placed in a 25 mL electrochemical cell for voltammetric

detection. All glassware was first cleaned in a base bath followed by soaking in 1 M nitric acid and was rinsed numerous times with deionized water before use.

All reagents were purchased from Fisher Scientific unless stated otherwise. Sodium acetate trihydrate (NaOAc) was dissolved and the pH adjusted (pH 5.0 unless stated otherwise) with acetic acid to make 0.1 M NaOAc buffer. The buffer contained appropriate amounts of gallic acid (0.2 mM unless stated otherwise) and vanadium standard solution. Stock solutions of 0.356 M potassium bromate (Mallinckrodt) in 0.1 M NaOAc buffer were prepared by dissolving the appropriate amounts of each in deionized water and adjusting pH to 5.0. Stock solutions of vanadium (5000 mg L⁻¹) were prepared by dissolving sodium metavanadate in a small amount of water and nitric acid (HNO₃) and diluting the solution to the final concentration with 5% HNO₃ or obtained from commercially available AA standards (1000 mg L⁻¹, Ricca). Vanadium standards were made by adding the appropriate volume of stock solution to prepared buffer solutions. Buffer solutions were used for a maximum of one week and stored at 4 °C when not in use. The bismuth plating solution, containing 20 mM Bi, 0.5 M potassium bromide (KBr) and 1 M hydrochloric acid (HCl), was prepared by dissolving bismuth needles (99.998%, Alfa Aesar) in 500 µL of concentrated nitric acid (HNO₃) and adding this to a solution of potassium bromide (KBr) and HCl. Polystyrene solution (1% w/w) was made by dissolving polystyrene pellets (Scientific Polymer Products, Inc., approx Mw = 235,000) in toluene or hexanes with stirring. Mercury plating solutions (400 mg L⁻¹) were made by dilution of a 1000 mg L⁻¹ AA standard solution (in HNO₃, Fisher).

Procedure

Mercury coated gold micro-wire electrodes (MWEs) were produced using previously published procedures [15,16]. Briefly, 100 µm gold wire (99.99%, Aldrich) was cut into approximately 2 cm pieces and inserted into the end of a disposable 200 µL pipette tip. A small amount of silver conducting epoxy was placed on the end of a copper wire (Fisher) and inserted into the top of the pipette tip until it nearly reached the end of the tip. The copper wire was turned until the gold wire also rotated to ensure electrical connection. The tip was then passed through a flame to melt and seal the plastic to the gold wire. The exposed gold wire was then cut before use to approximately 2–3 mm in length. Mercury was coated from a solution of 400 mg L⁻¹ Hg by applying a potential of –0.4 V for 600 s. The electrodes were then activated several times by applying a –3 V potential for 3 s. Electrodes could be used for several days without significant losses in sensitivity and mercury could be re-deposited several times on each Au wire.

Acetate buffer (19 mL) with gallic acid (0.2 mM) was pipetted into a voltammetric cell. All solutions were deoxygenated by bubbling with nitrogen gas for 5 min before analysis. Potassium bromate solution (1 mL) was added at the time of measurement. The micro-wire electrode was activated inside the analyte solution at –3 V for 3 s by adding a preconditioning step in the CHI software. Preconcentration times were also built into the scan using the CHI software and stirring was applied followed by a 15 s period with no stirring before the scan. Differential pulse voltammetry (DPV) scans were then obtained (0.05 V amplitude, 0.05 s pulse width, 0.05 s sample width, 0.2 s pulse period). A cleaning step (–0.9 V, 20 s, with stirring) was applied in buffer solution between samples.

Bismuth film electrodes were prepared by electrodepositing bismuth on a polished glassy carbon electrode (Cypress Systems, Lawrence, KS) in the Bi plating solution. A potential of –0.25 V was applied for 300 s without stirring to reduce Bi(III) ions and form a visible thick film on the electrode surface. Polystyrene coatings were put on top of the Bi to protect the fragile film, by pipetting 5 µL of 1% polystyrene solution and 5 µL dimethylformaldehyde, similar to previous reports for Nafion films [17]. Once dry, the film was cured with a heat gun for approximately 1 min and allowed to cool before use.

Electrochemical detection was accomplished by DPV. Potassium bromate solution (1 mL) was added to standard solutions (19 mL) directly before measurement. The electrode was held at a potential of -0.35 V with stirring to deposit the V-GA complex on the surface of the working electrode. To do this, the stripping mode in the CHI software and a time of 600 s were set. The stirring was turned off 15 s before the start of the potential scan. The DPV scanned from -0.35 to -0.85 V (0.05 V amplitude, 0.05 s pulse width, 0.05 s sample width, 0.2 s pulse period) to generate the voltammetric scans. The electrode was cleaned in buffer solution by applying a potential of -1.2 V for 40 s with stirring. The resulting plots were background fitted and subtracted using CHI software.

Results and Discussion

Gallic acid as ligand for CAdSV analysis of V(V)

CAdSV for the detection of vanadium has been reported at bismuth thin film electrodes using chloranillic acid (CAA) as the complexing ligand with a detection limit of 200 ngL^{-1} with 10 min accumulation times [10]. Other ligands such as catechol, cupferron, and gallic acid (GA) have been investigated for CAdSV detection of V [3,12,13,18,19]. CAdSV using GA ligand was reported to have sub nM detection limits at mercury drop electrodes [13]. GA, to our knowledge, has not been used on either mercury coated gold microwire electrodes or Bi electrodes.

Mercury-coated gold microwire electrode and its use in V(V) CAdSV

MWEs have recently been developed for CAdSV detection of iron-dihydroxynaphthalene complex using bromate as an oxidant [15]. Gold forms amalgams with mercury. The alloys are more stable and are more sensitive electrodes upon multiple amalgamations [16]. MWEs were used until there was a notable decrease in sensitivity after which they could be redeposited and used again many times. It is essential to calibrate the electrode each time it is used as the sensitivity does change between days or Hg depositions. These electrodes are easier to make than labor-intensive micro-disc electrodes and offer better sensitivity due to the larger area of the electrode [16]. MWEs have an overpotential for the direct reduction of bromate, which allows for catalytic detection of complexes at more positive potentials than the potential of direct bromate reduction. Additionally, the small size of the electrode produces a steady-state mass transport condition and resulting constant current with little or no stirring during the deposition step. A further advantage of MWEs is that they have been demonstrated to work in flow injection systems for CAdSV detection of iron [15]. This method could be easily adapted to flow analysis of V for increased automation, and perhaps an on-line preconcentration technique could be coupled if higher sensitivity were needed [20]. Initial experiments at a $100 \text{ }\mu\text{m}$ diameter electrode showed a CAdSV catalytic V-GA peak in the presence of bromate at -0.55 V similar to that reported on a hanging mercury drop electrode [13]. The response increased linearly with added concentration of V in the $50\text{--}1000 \text{ ngL}^{-1}$ range.

Optimization of the catalytic signal

The experimental conditions were optimized by changing various parameters of the detection method. The standard conditions of pH 5.0 (acetate buffer), $100 \text{ }\mu\text{M}$ GA, 10 mM BrO_3^- , a 120 s deposition at -0.3 V were kept constant while each parameter was optimized. A 3 s activation at -3 V was used immediately prior to DPV scans.

Variation of pH showed that the peak current was most sensitive at pH 5 (Fig. 1A). This is consistent with the reported work at mercury drop electrodes. The pK_a of GA is 4.45, and thus at $\text{pH} > 4.5$, an increase in pH leads to an increase in gallate anion concentration which in turn increases the formation of the V-GA complex. However, at $\text{pH} > 5$ the dissociation of metavanadate increases as well, and thus it is expected that less V-GA complex would form

[13]. The peak potential also shifts in a more negative direction with increase in pH. Therefore, it is reasonable that pH of 5 in 0.1M acetate buffer was found to be optimum.

Next, the concentration of gallic acid was optimized (Fig. 1B). Increase in the concentration of GA from 0 to 1 mM showed a large increase at first, which leveled off at higher concentrations. For further results, 200 μ M GA was used as there was no significant gain in peak current at higher concentrations.

The sensitivity increased with increased concentration of bromate (Fig. 1C). There was little change between 0 and 7 mM. Between 7 and 15 mM, the increase was more dramatic, followed by a smaller change after that. Thus, 15 mM was chosen as the optimum concentration of bromate. It is important to note the importance of adding bromate to the solution at the time of measurement. Buffer solutions containing GA change color from clear to a slight yellow color after the addition of bromate. The solutions were only stable for a short time after the addition of the oxidant. Therefore, the bromate solution was added to each sample individually before measurement and the measurement was completed within 3 min of the addition. New solutions are required for each measurement.

The deposition potential was optimized by varying it from -0.2 to -0.4 V. Peak current remained statistically constant producing a satisfactory stripping wave from -0.2 to -0.325 V. At potentials >-0.3 V, the deposition potential was closer to the start of the peak and in the case of -0.4 V, the peak started immediately at the onset of the scan reducing the effect peak height and peak area. All accumulations after this point were at -0.275 V. The deposition time was also investigated (Fig. 1D). The accumulation time was increased from 10–420 s at -0.275 V. The peak current increases linearly from 10–100 s and begins to level off afterwards. Accumulation times of >300 s appear to make little difference.

Performance

MWEs were used to generate calibration plots using the optimized parameters. Fig. 2 shows the calibration in the $0-1000 \text{ ngL}^{-1}$ range. At low concentrations two peaks are evident, one at -0.55 V and the other at -0.65 V. At higher concentrations, the more positive peak dominates. While the reason for this phenomenon is unknown, one possible explanation is that the more negative peak is comparable to the postwave adsorption peak first studied by Brdicka [21] and later by Wopschall and Shain [22]. They observed a diffusive peak from the bulk solution and a postwave adsorption peak from the species adsorbed to the surface of the electrode. While the current phenomenon is not strictly analogous, as it is an adsorptive technique and the diffusive peak should not be significant, similar voltammetric behavior could be envisioned. Two forms of the complex could exist, one from a strongly absorbed monolayer directly on the surface of the electrode and the other from weakly absorbed multi-layers. At low concentrations, the relative amount of both species is evidently more or less equal and thus two peaks are evident. At higher concentrations, the surface of the electrode is saturated with the complex and the more positive peak from the multi-layer absorption dominates. Given that this system is catalytic, the chemical reaction of the oxidant with the monolayer complex might also be limited when the multilayer species is more prevalent. The multilayer complex would consume the oxidant in the diffusion layer, leading to selective catalytic peak enhancement for that complex. With no oxidant, there would be only non-catalytic reduction current for the monolayer species. Accordingly, it was found that the area of both peaks was best for generating calibration plots when two peaks were present. A similar response phenomenon was seen at a HMDE with CAA as the ligand for V detection. In this study, two peaks were observed when the concentration of CAA was lower than that of V(V). As the concentration of ligand was increased, the more positive peak disappears and the negative peak gets stronger [11]. While this could have some implications about the ratio of GA-V in the current study, it is unlikely due to the fact that GA is present in great excess (10^4 M).

The calibration data were fit using both linear and hyperbola equations (Fig. 2B). The calibration in Fig. 2 yielded the following linear plot: peak area ($V\mu A$) = $0.5(0.2) + 1 \times 10^{-2}(0.04 \times 10^{-2}) C_{V(V)}$, ($R^2 = 0.9927$). Repetitive scans of a 50 ngL^{-1} standard (supplemental materials) produced reproducible reduction peaks after two min accumulation times with a limit of detection of 0.88 ngL^{-1} based on 3 times the standard deviation. Even with extended accumulation times (10 min), bismuth electrodes could not produce the sensitivity of mercury-based counterparts [10]. As noted earlier, MWEs offer comparable detection limits to mercury-drop electrodes while using much less mercury [11]. Furthermore, mercury forms an alloy with gold making the mercury films more stable and safer than mercury drop or films electrodes. For these reasons we believe that mercury-coated microwire electrodes are superior for applications where lower detection limits are required.

Several common inorganic anions were tested for their interference on V CAdSV detection. The effect of various metal ions at concentrations 20 times that of a 500 ngL^{-1} V sample is shown in Table 1. While most metal ions did decrease the overall current of the V CAdSV peak, the peak was, however, still present in all cases. Mo(VI) showed the most significant change to the background response with what appears to be two small non-catalytic peaks (-0.28 and -0.7 V). As is expected, the model surfactant Triton X-100 produced a significant decrease in the peak current due to the fact that it absorbs at negative potentials [23]. An in-depth interference study at HMDE for the same GA-V CAdSV system tested 28 inorganic species and showed that organic acids such as citric acid and oxalic acid caused the stripping wave to disappear [13] (see supplemental material for summary). Because of the matrix effect on the overall sensitivity of the measurement, it is suggested that the sensitivity of each sample be ascertained separately by means of the standard addition method.

To validate the accuracy of the new technique, an expired vanadium AA (exp. date 1987) standard was quantified by both flame AA and the proposed protocol using standard addition of a certified AA standard (Table 2). The AA analysis resulted in a concentration of $1078 \pm 2 \text{ mgL}^{-1}$. After a 10^6 times dilution to ngL^{-1} level, the MWE technique resulted in a concentration of $1098.6 \pm 0.05 \text{ ngL}^{-1}$, a difference of 1.9%. River water samples were collected from the Emory river near Harriman, Tennessee (see supplemental materials for sample information). River water was acidified with nitric acid, filtered, and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and the new CAdSV method for V content. For the electrochemical analysis, river water was diluted to ngL^{-1} concentrations to make solutions containing buffer components. All conditions were the same as those reported in the optimization procedure. A vanadium level of $31.13 \pm 0.05 \mu\text{gL}^{-1}$ was found in the original water sample by use of the standard addition method (4 additions of $25\text{--}100 \text{ ngL}^{-1}$ V(V) to diluted ($\sim 50 \text{ ngL}^{-1}$) river water) resulting in a linear response: peak height (μA) = $-0.18(0.01) + 3.5(0.2) \times 10^{-3} C_{V(V)}$ ($R^2 = 0.9934$) (Fig. 3). This result was validated by the ICP-OES (309.31 nm) concentration of $29.1 \pm 4.6 \mu\text{gL}^{-1}$ by standard addition method (Table 2). These results are promising for the feasibility of use for these electrodes in possible field-testing applications.

Polystyrene-coated bismuth film electrodes

Bismuth thin film electrodes were first used in an attempt to eliminate the need for mercury-based electrodes. They exhibit similar properties of mercury-based electrodes, such as the high overpotentials for hydrogen evolution needed for CAdSV. A variety of CAdSV techniques for V detection using several ligands at mercury-based electrodes have been reported with detection limits as low as $4.9 \times 10^{-12} \text{ M}$ [3,12,13,18,19]. There are a number of recent papers and reviews describing the use of thin film bismuth electrodes, including CAdSV techniques for detection of chromium and vanadium [10,24–27]. We studied the use of Bi thick film electrodes for CAdSV analysis of V(V) using both CAA and GA with a hope to achieve a lower detection limit than that previously reported at bismuth thin films [10]. In addition, we have

been interested in making more reproducible and robust Bi films on glassy carbon electrode (GCE) substrates.

Thick Bi films were plated using more concentrated Bi(III) (0.02 M) solutions to produce visible films on the electrode surface. The thicker films were found to be more reproducible than thin films. However, when directly used, the films were found to be fragile and had a tendency to degrade (Fig. 4A and 4B). In addition, when using CAA as the complexing ligand, the complex was difficult to remove from the electrode surface to regenerate the electrode for subsequent scans. When buffer solution without V was run first, there were no catalytic peaks. After exposing the electrode to CAA-V complex and following a cleaning step, the buffer produced a response (Fig. 4C and 4D). Only after repeating the cleaning step numerous times could the complex be removed.

The pretreatment of biological samples often requires harsh conditions and the use of chemicals such as hydrogen peroxide, a strong oxidant that is known to oxidize Bi. We were interested in robust electrodes that can tolerate residual H_2O_2 [9] and can resist fouling of the Bi surface by biological materials that might be present in the pretreated samples. We have thus investigated the use of a protective layer on the Bi surface to reduce degradation and fouling.

Polymer films have been widely used as protective coatings on film electrodes. Nafion films provide several important advantages including added mechanical stability, increases in sensitivity, and resistance to fouling [17]. Nafion is a linear polymer with sulfonic acid and carboxylic acid groups developed by DuPont in 1962 [28]. The films are chemically and thermally inert and can form thin membranes, and the sulfonate and carboxylate groups can interact with cations by partial or total exchange. However, the anionic polymer will adversely influence the adsorption of the anionic vanadate ion. Indeed, a Nafion film coated from a 1% Nafion solution on a Bi film electrode caused a dramatic decrease in the catalytic reduction peak for V(V)-V(IV).

Polystyrene films were investigated as a non-ionic alternative to Nafion films. A bare GCE was compared to one coated with a thin polystyrene film to determine what effect the film would have on the electrochemical properties (Fig. 5). There was a slight decrease in sensitivity in the cyclic voltammetry of a standard solution of potassium ferrocyanide, due to the decrease in the effective area of the GCE from polystyrene coverage. Thick Bi film electrodes coated with polymer showed consistent and reproducible results.

The use of gallic acid (GA) and thick Bi film electrodes gave reproducible results for V concentrations at $\mu\text{g L}^{-1}$ levels with accumulations times of 120 s (Fig. 6A). These results are comparable to results obtained from the CAA complexing ligand at Bi-based thin film electrodes. However, irreversible adsorption of the GA-V complex was not observed at our thick Bi films electrodes as was observed with the CAA-V complex (Fig 4D). However, detection at ng L^{-1} level was only possible with extended accumulations times (10 min). The DPV scans were background fitted and subtracted to obtain the six point calibration plot (Fig. 6B) with a linear response: peak current (μA) = $0.0 (0.1) + 3.6(0.2) \times 10^{-3} C_{\text{V(V)}}$ ($R^2 = 0.990$). While using GA as the complexing ligand solved the problem of irreversible adsorption seen with CAA at thick film electrodes, detection of ng L^{-1} levels required extended accumulation times. In comparison, mercury-coated microwire electrodes require a much shorter accumulation times to achieve similar sensitivity (120 s).

Conclusions

The detection of ultra-trace vanadium (V) was successful using both mercury-coated gold micro-wire and bismuth film electrodes. The use of GA as the complexing ligand allowed for the easy removal of its V complex from Bi electrodes and ng L^{-1} level detection with extended

accumulation times. The parameters for detection at MWEs were optimized for pH, concentration of ligand and oxidant, deposition potential and deposition time. MWEs offer detection limits that rival that of pure mercury-based electrodes. However, these electrodes eliminate mercury waste and stabilize it by amalgamation with gold. They have been demonstrated for use in tap water samples without pretreatment and were validated by comparison of AA results. Bismuth-based electrodes have limited lifecycles, insufficient detection limits for vanadium, and are not easily automated for clinical based trials of the detection of metals in biological samples. MWEs are robust, have low detection limits, and have been demonstrated to be compatible with flow injection analysis [15]. We are investigating pretreatment of biological samples for V analysis and the use of the electrochemical methods here to determine vanadium concentrations in these samples.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. Optimization of the signal of vanadium detection by CAAdSV at a MWE: (A) Effect of varying pH; (B) concentration of GA; (C) bromate concentration; (D) deposition time. In general the

conditions were 0.1 M sodium acetate buffer, pH 5.0, 100 μ M GA, 10 mM bromate, -0.3 V accumulation potential, and 120 s deposition time.

Fig. 2.
 (A) Differential pulse voltammograms (-0.05 V amplitude, 0.05 s pulse width, 0.05 s sample width, 0.2 s pulse period) for increasing levels of vanadium, -0.275 V accumulations for 120 s; (B) Hyperbola fit.

Fig. 3. Standard addition of V to Emory river water samples. Conditions as in Fig. 2A with background fitting and subtraction.

Fig. 4.

(A) Bi film electrode on GCE, 60 s deposition, -0.25 V, 0.02 M Bi(III); (B) The Bi electrode after exposure to a solution containing residual H_2O_2 ; (C) CAdSV detection of V-CAA complex accumulation at -0.35 V; (D) Comparison of buffer DPV response (-0.05 V amplitude, 0.05 s pulse width, 0.05 s sample width, 0.2 s pulse period) at a freshly prepared electrode and buffer response after exposure to V-CAA containing solutions, showing the extent of irreversible adsorption.

Fig. 5. Comparison of current response of $[\text{Fe}(\text{CN})_6]^{3-}$ at bare glassy carbon and polystyrene coated electrodes (0.1 V/s scan rate, 0.001 V sample interval).

Fig. 6.

(A) V-GA CAdSV detection at polymer-coated Bi film electrode, 120 s accumulation; (B) V-GA CAdSV detection, 600 s accumulation with background fitting and subtraction (-0.05 V amplitude, 0.05 s pulse width, 0.05 s sample width, 0.2 s pulse period).

Table 1

Effect of interferences on CAdSV determination of V with GA

Interference	Peak influence	Recovery of $0.5 \mu\text{g L}^{-1}$ V together with $10 \mu\text{g L}^{-1}$ interference
Ni (II)	Increase peak current	$< 1\sigma$ of $0.5 \mu\text{g L}^{-1}$ mean
Cr (VI)	Decrease	75%
Mo (VI)	New peak at -0.7 V and baseline shift at -0.3 to -0.4 V	83%
Fe (III)	Decrease	$< 1\sigma$
Al (III)	Decrease	73%
Se	Decrease	79%
As	Decrease	80%
Sn	Decrease	67%
Triton X-100 (50 mgL^{-1})	Completely suppressed	---

Determination of vanadium by standard addition

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