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Determination of vanadium in sea water by catalytic adsorptive cathodic stripping voltammetry

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Abstract

The sensitivity of adsorptive cathodic stripping voltammetry (CSV) to vanadium is much improved by inclusion of a catalytic effect. The deposition step is based on the adsorptive accumulation of complex species with catechol on a hanging mercury drop electrode. The reduction current of the adsorbed complex is catalytically enhanced by addition of bromate. This effect is utilised to develop a sensitive method to determine vanadium in natural waters including sea water. Optimum response was obtained at pH 6.6 in the presence of 20 mM bromate and 0.1 mM catechol; the deposition potential was -0.1 V and the square-wave modulation (50 Hz) was used. The limit of detection was 0.07 nM vanadium using a deposition time of 120 s and 0.6 nM at a deposition time of 15 s.

Key words: Catalytic methods; Stripping voltammetry; Sea water; Vanadium; Waters

1. Introduction

Adsorptive cathodic stripping voltammetry (CSV) is a useful method to determine trace elements in natural waters combining excellent sensitivity, selectivity, accuracy and precision with low cost of instrumentation and maintenance. Applications of CSV and its potential for natural water analyses have recently been reviewed [1].

Vanadium occurs in sea water in a concentration range from 10 to 40 nM, with average levels of ~ 32 nM [2,3]. Several methods have been proposed for the determination of vanadium in

natural waters, most of which require prior pre-concentration steps (without a prior preconcentration step such as requiring the use of ion-exchange or co-precipitation) which prolong the analysis duration and increase the risk of sample contamination or loss of analyte. Adsorptive stripping procedures allow the determination of various trace elements directly in untreated sea water, leading to short analysis times and sub-nanomolar to picomolar detection limits. This method was therefore used to develop a sensitive procedure to determine vanadium in sea water.

The principle of adsorptive CSV is the measurement of the reduction current of either the element or the ligand preceded by adsorptive collection on the electrode surface of a complex of the element with an added specific ligand [1].

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Several ligands including catechol [4], 5-Br-PADAP [5,6] and solochrome violet RS [7] have been used to accumulate vanadium as complexes by adsorption on the mercury electrode surface. It has been shown that vanadium can be determined successfully in sea water using one of these (catechol), but the sensitivity is not great and accurate analyses would require a deposition time of several minutes.

The CSV sensitivity can be increased greatly by the inclusion of a catalytic effect; this has been shown to work for several elements when the reduction step involved only one electron [1] and has been used with good advantage for the determination of titanium [8], iron [9], chromium [10,11] and platinum [12] in sea water. The reduction of vanadium in the presence of catechol involves a single electron reduction step from V(V) to V(IV) and its catechol complex is adsorbed on the mercury drop electrode [4]; it is therefore a good candidate for catalytic CSV.

It has been claimed that “ultra trace levels” of vanadium can be determined by catalytic CSV preceded by adsorptive collection of its complex with cupferron [13] giving a peak at ~ -0.1 V. The stated reduction potential is unexpectedly positive as the reduction potential for uncomplexed vanadium is situated at a more negative potential at ~ -0.3 V [4]. One would expect the complexed peak to be located at a more negative potential rather than at a more positive potential due to a combination of complex stabilisation and adsorption stabilisation. The potential of the peak would in any case preclude the application of this method to solutions containing chloride due to a negative shift of the mercury wave which causes a large background current at potentials > -0.05 V in sea water. During preliminary experiments using cupferron and vanadium using the published conditions [13] we were not able to reproduce the vanadium peak in either pure water or sea water; a peak which looks similar to that shown for vanadium could be produced by allowing a small amount of dissolved oxygen to diffuse into the deaerated solution, suggesting that the oxygen peak may have been erroneously identified as a reduction peak of vanadium. A vanadium peak could be obtained in the presence of

cupferron at much enhanced vanadium levels (100 nM) at the more negative potential of -0.7 V without analytical usefulness as the sensitivity is poor.

We therefore set out to improve the voltammetric determination of vanadium in the presence of catechol by the inclusion of a catalytic effect which is reported in this paper. Several ligands (catechol, salicylaldoxime, tiron, 4-(2-pyridylazo)resorcinol (PAR), 1-(2-pyridylazo)-2-naphthol (PAN), *N*-benzoyl-*N*-phenylhydroxylamine and cupferron) and oxidants (bromate, chlorate and perchlorate) were tested, but only the successful results obtained in the presence of catechol and bromate are reported.

2. Experimental

2.1. Apparatus and reagents

The voltammetric experiments were carried out with an Autolab PSTAT10 voltammeter (Eco Chemie) connected to a Metrohm 663VA hanging mercury drop electrode (HMDE). The reference electrode was Ag/saturated AgCl/3 M KCl and the counter electrode was a Pt rod. Solutions in the voltammetric cell were stirred by a rotating PTFE rod. The potentiostat was controlled by an IBM-AT compatible computer (286 Intel processor) using a compiled BASIC programme (GPES31 from Eco Chemie). The mercury was triple-distilled and the drop size of the HMDE was 0.31 mm^2 . pH values were determined with a Metrohm 605 pH meter and a Metrohm combined glass pH electrode.

A stock solution of 10^{-4} M vanadium(V) was prepared by dilution of BDH standard solution (1000 mg/l) for atomic absorption spectroscopy, and acidified with $10 \mu\text{l}$ of 11.4 M hydrochloric acid per 10 ml solution. An aqueous stock solution of 1 M PIPES (piperazine-*N,N'*-bis(2-ethanesulfonic) acid, from Sigma) was prepared by dissolution of its monosodium salt in 0.5 M ammonia hydroxide (BDH, AristaR grade). Addition of $200 \mu\text{l}$ of the PIPES solution to 10 ml sea water gave a pH of 6.6. Stock solutions of 0.2 M potassium bromate (BDH, AnalaR) and 0.1 M

catechol (BDH, AnalaR) were prepared by dissolving the respective compounds in water. Water used for dilution of the reagents and for rinsing of sample containers and the voltammetric cell was purified by reverse osmosis (Milli-Ro) and deionisation (Milli-Q). A mixed reagent solution containing 1 mM catechol and 0.2 M potassium bromate in 200 ml water was heated and boiled (180 s) in a microwave oven; the resultant solution was pink coloured due to oxidation of the catechol to orthobenzoquinone.

Sea water used for the optimisation experiments originated from the Menai Straits (Irish Sea). This sea water was UV-digested (3 h) using a 1000-W UV lamp in the presence of 9 mM hydrogen peroxide to remove potentially interfering surface active compounds. Vanadium and other metals present as traces in the sea water were removed by passing the UV-digested sea water through a column packed with ca. 3 ml Chelex-100 resin (in the ammonium form) at a flow rate of 1 ml/min to produce sea water with a low vanadium level; this sea water was used for the determination of the limit of detection of vanadium and for other experiments where indicated.

2.2. Procedure to determine vanadium in sea water

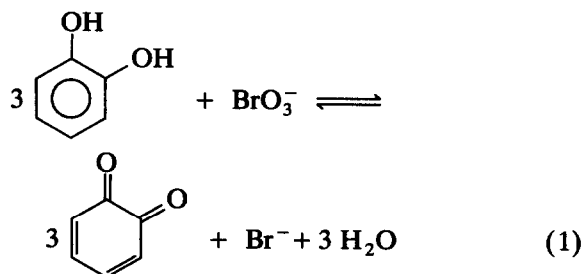
An aliquot of 10 ml of sea water was pipetted into the voltammetric cell and 1 ml of the mixed reagent solution was added giving final concentrations of 10^{-4} M catechol and 0.02 M bromate. The pH was adjusted to 6.6 by addition of 200 μ l of the 1 M PIPES buffer, and the solution deaerated by purging with water-saturated nitrogen (3 min). A new mercury drop was extruded and the deposition potential was set to -0.1 V for a period of 15 s, whilst the solution was stirred at 2500 rpm. Then the stirrer was stopped and the potential was set to -0.4 V for a period of 10 s, whereafter the potential was scanned towards more negative potentials using the square-wave modulation. Scan parameters were: square-wave frequency: 50 Hz; square-wave amplitude: 25 mV; potential step: 2.4 mV (scan rate, 120 mV s $^{-1}$). A peak corresponding with the catalysed reduction of vanadium appeared at -0.74 V. The peak

height (nA) was used as a measure of the reduction current. Each measurement was repeated at least twice; the measurements were repeated again after standard additions of vanadium to the sample to calibrate the CSV sensitivity and check for linearity of response.

3. Results and discussion

3.1. An investigation into the catalytic adsorptive stripping process

Preliminary experiments on CSV of vanadium in the presence of catechol in pH 6.6 sea water indicated the presence of a vanadium peak at ~ -0.7 V due to the reduction of vanadium(V) in the adsorbed complex of vanadium with catechol to vanadium(IV) [4]. The sensitivity was much improved by the addition of up to 20 mM bromate to the solution causing the peak current to increase and the peak potential to shift towards more negative potentials (details given below). Repeated measurements of the CSV peak height of vanadium in the presence of 20 mM bromate and 0.1 mM catechol preceded by 15 s deposition at -0.1 V revealed that the peak height was unstable in presence of the bromate, increasing gradually with time at a constant concentration of vanadium, reaching a further four-fold magnification over a period of 2 h. The effect could be accelerated and brought to completion by preparing a mixed reagent solution containing 1 mM catechol and 0.2 M bromate: heating of this stock solution in a microwave oven as described in the Methods section caused the catechol to become oxidised to orthobenzoquinone, imparting a pink colour to the solution typical of orthobenzoquinone [14] according to the following reaction:



Addition of the oxidised catechol (orthobenzoquinone) and bromate produced stable CSV peak currents for vanadium. It is therefore likely that the initial unstable peaks were caused by the slow and gradual oxidation of the catechol by the bromate. The oxidised catechol (orthobenzoquinone) stock solution premixed with bromate was therefore used for further experiments.

Cyclic voltammetry of catechol in an aqueous solution of PIPES pH buffer (pH 6.8) without vanadium revealed the presence of an anodic peak at +0.16 V due to the oxidation of catechol to orthobenzoquinone. Cyclic voltammetry of catechol using the HMDE and a glassy carbon electrode (GCE) can be compared in Fig. 1A. The redox potential of the catechol/orthobenzoquinone couple at the HMDE (+0.16 V) is in good agreement with that (+0.18 V) reported for pH 7.0 [15]. The redox couple was not fully separated from the mercury oxidation wave and was situated on the shoulder of the mercury(II)/mercury(0) redox couple. An anodic and a cathodic peak could be identified, with peak potentials differing by ~ 80 mV, showing that the catechol/orthobenzoquinone redox reaction was reversible at the mercury electrode. This means that orthobenzoquinone (when added to the bulk solution instead of catechol) is reduced back to catechol (and available for complex formation) at the electrode surface at all times at potentials $< +0.16$ V during the deposition and scanning steps of the analytical procedure, as opposed to in the solution as in the previous work [4]. It is interesting that the sensitivity was much improved under these conditions.

Separate cyclic voltammetric experiments of catechol in PIPES buffer using a GCE produced a much larger potential difference between the anodic (+0.47 V) and cathodic (0.0 V) peak potentials showing that the redox couple was poorly reversible at this surface (Fig. 1A).

Cyclic voltammetry was used to evaluate the reaction mechanism. Cyclic voltammograms for 10 nM vanadium in pH 6.6 sea water in the presence of 10 mM PIPES, 10^{-4} M catechol and 20 mM bromate are shown in Fig. 1B. The first scan was carried out after 60 s adsorption at -0.1 V at a scan rate of 50 mV s^{-1} , and was

immediately followed by a second scan without prior adsorption. A large reduction peak (300 nA at a vanadium concentration of 10 nM) was obtained at -0.84 V due the reduction of vanadium(V) to vanadium(IV) on the forward scan towards more negative potentials. The peak at -0.84 V was found to increase with the adsorption time in accordance with a process in which the current is predominantly derived from the reduction of an adsorbed compound. The peak was not present at this low level of vanadium (10 nM) in the absence of bromate but a reduction peak for the adsorbed complex of vanadium with catechol is known to appear at a more positive potential of ~ -0.7 V at a much higher concentration (mM level) of vanadium in otherwise similar conditions [4]. A cathodic peak apparent at ~ -0.45 V (Fig. 1B and C) was due to reduction of an adsorbed complex of molybdenum which is present at ~ 100 nM in sea water.

Interestingly a cathodic (reduction) peak appeared instead of an expected anodic (oxidation) peak in the reverse scans (towards more positive potentials) from -1.2 to -0.1 V (Fig. 1B). This observation is consistent with a reaction mechanism in which the peak current for the reduction of vanadium(V) to vanadium(IV) is catalytically enhanced and where the reduced (vanadium(IV)) complex with catechol does not adsorb on the mercury surface. Diffusion of the vanadium(IV)–catechol away from the electrode surface causes the peak current of the forward scans to drop steeply at potentials more negative than -0.84 V causing the peak-shape of the reduction wave (Fig. 1B) instead of the stepwise increase to be expected from a diffusion current. The diffusion of the vanadium(IV) from the electrode surface causes the main cathodic peak to decrease in the second and subsequent negative-going potential scans (Fig. 1B).

Cyclic voltammetry of the vanadium complex with catechol showed that the cathodic peak was asymmetric. The asymmetric peak shape illustrates that a diffusion component (that of the oxidant bromate) is important as a reversible reduction peak entirely due to the reduction of an adsorbed compound would be symmetric. Cyclic voltammograms at scan speeds of 5, 50 and

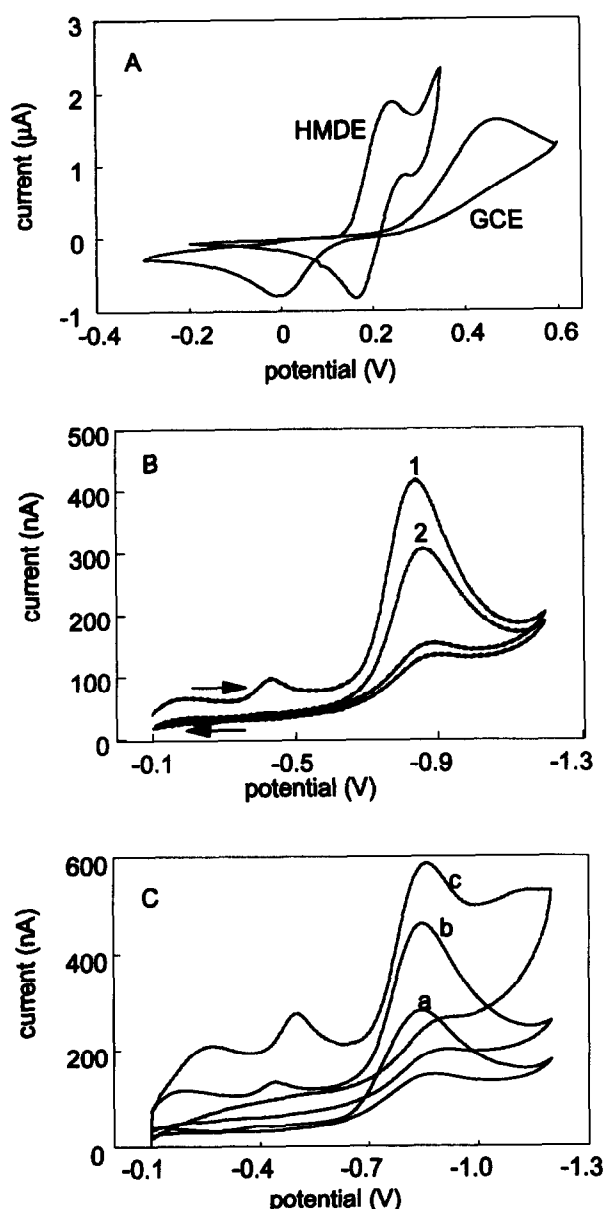


Fig. 1. Cyclic voltammetry of free catechol (A) and of catechol complexes with vanadium (B and C). (A) Cyclic voltammetry of free catechol in 0.02 M PIPES buffer using an HMDE (2 mM catechol) and a GCE (0.2 mM catechol). The scans were not preceded by deposition. The scan rate was 10 mV/s. (B) Consecutive cyclic voltammograms after 60 s of deposition from sea water containing 10 mM PIPES buffer (pH 6.6), 10 nM vanadium(V), 20 mM potassium bromate and 10⁻⁴ M catechol. Deposition potential, -0.1 V; scan speed, 50 mV/s. (C) Cyclic voltammograms of 10 nM vanadium at scan rates of 5 (a), 50 (b) and 500 (c) mV/s; solution composition as in (B).

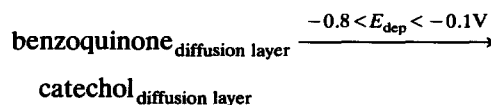
500 mV s⁻¹ showed that the asymmetry increased with increasing scan rate due to increasing diffusive and capacitive components (Fig. 1C). The reduction current of adsorbed species should increase linearly with the scan rate as the reducible charge is constant, whereas a linear relationship with the square root of the scan rate is valid for diffusion currents [16]. Interestingly a plot (Fig. 2A) of the peak height of the vanadium peak as a function of the square root of the scan rate is linear at scan rates < 50 mV s⁻¹ indicating that the effect of the diffusion current (of the bromate) on the peak height is predominant at these scan rates. The linearity breaks down at greater scan rates giving less peak height than expected, presumably due to the slowness of the catalytic process (see below).

The catalytic nature of the vanadium(V)/(IV) redox reaction in the presence of bromate is illustrated by means of a diagnostic test [17] utilising a plot of ($i_{\text{cathodic}} \times v^{1/2}$) versus v (Fig. 2B), where i_{cathodic} is the peak current of the vanadium peak and v the scan rate. At low values of v a comparatively large amount of bromate diffuses towards the electrode surface reoxidising the vanadium(IV) and leading to current values higher than expected from the reduction of vanadium(V) alone, thus causing the shape of the plot shown in Fig. 2B which is typical for catalytic processes [17].

3.2. Reaction mechanism

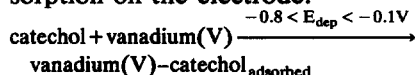
The proposed mechanism is as follows.

Adsorption step at -0.1 V: Diffusion of orthobenzoquinone and vanadium to the electrode surface where the orthobenzoquinone is reduced to catechol, forming an adsorptive complex with vanadium:

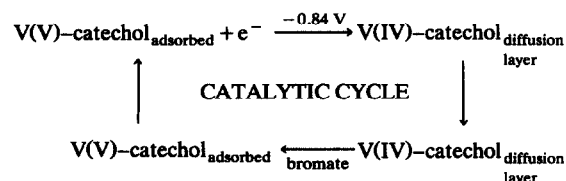


The catechol is retained in the reduced form at the electrode surface under the influence of the applied potential and furthermore the oxidation kinetics with the bromate were quite slow, requiring microwave boiling to reach completion within

minutes. The formed catechol is then available for complex formation with vanadium and adsorption on the electrode:



The vanadium in the adsorbed complex with catechol is reduced to vanadium(IV) at potentials < -0.84 V in the subsequent potential scan. The vanadium(IV) is chemically reoxidised to vanadium(V) by the bromate and is available again for repeated reduction, thus causing the catalytic increase in the reduction current:



3.3. Effects of varying the solution composition on the CSV of vanadium

Preliminary experiments comparing linear sweep voltammetry with square-wave voltammetry showed that the peak shape and sensitivity were improved by using the square-wave modulation which was therefore used for analytical purposes.

The optimal concentration of bromate was determined by CSV after deposition at -0.1 V at two different deposition periods (20 and 60 s) at bromate concentrations increasing from 0 to 30

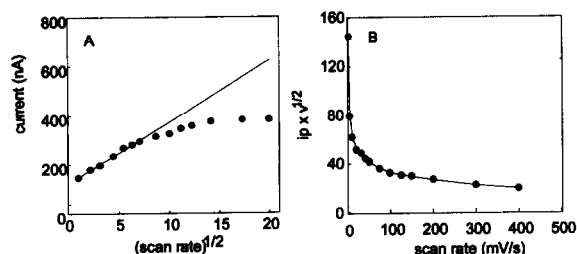


Fig. 2 Effect of varying the scan rate of cyclic voltammetry on the cathodic peak height of the vanadium complex of catechol. (A) The peak current versus the square root of the potential scan rate. (B) Diagnostic test for catalytic mechanisms (see text).

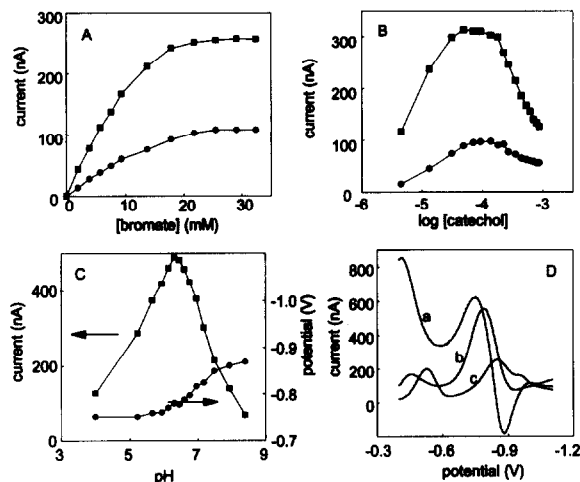


Fig. 3. Effect of varying the solution composition on the CSV sensitivity for 10 nM vanadium in UV-digested purified sea water: (A) Variation of the concentration of bromate using a deposition period of 20 (●) and 60 (■) s. (B) Variation of the catechol concentration using a deposition period of 20 (●) and 60 s (■). (C) Variation of the pH using a deposition time of 60 s. (D) CSV scans after 60 s deposition at pH 5.2 (a), 6.6 (b) and 7.5 (c).

mM at a constant concentration of 0.1 mM of oxidised catechol (orthobenzoquinone). It was found (Fig. 3A) that the peak height increased with increasing concentration of bromate, the increase levelling off at 20 mM bromate, whereas the peak potential did not vary significantly with the bromate concentration. A similar effect of the bromate concentration was obtained when this experiment was carried out using catechol but the peak potential was found to shift from -0.67 V in the absence of bromate towards more negative potentials (-0.76 V at 20 mM bromate). This potential shift occurred apparently already at low bromate concentrations when the catechol was added as orthobenzoquinone to the solution.

A concentration of 20 mM bromate was selected for further analytical studies as it produced good sensitivity. It would be possible to increase the sensitivity further by using higher bromate concentrations but the additional increase is small compared to that reached already, and a disadvantage is that a large volume of bromate has to be added: a volume of 1 ml of 0.2 M bromate is

added to 10 ml sea water to obtain the concentration of 20 mM.

The influence of varying the catechol (added as oxidized catechol) concentration in the presence of 20 mM bromate on the CSV peak height is shown in Fig. 3B. The sensitivity for vanadium was found to increase with the catechol concentration reaching a maximum at 0.1 mM whilst decreasing at higher concentrations. The peak potential shifted gradually from -0.78 V (at $5 \mu\text{M}$ catechol) to -0.76 V (at 0.9 mM catechol).

The effect of varying the pH on the CSV sensitivity for vanadium in sea water is shown in Fig. 3C. Greatest sensitivity was obtained at pH values between 6.3 and 6.6, whereas the sensitivity was much less outside this pH range: an increase in the pH caused the peak height to decrease strongly probably due to hydrolysis of vanadium(V), whereas pH values below 6.0 caused a decrease in the peak height as well as a asymmetric peak shape possibly as a result of enhanced sensitivity for molybdenum which appears at a more positive potential. The effect of the pH on the peak shape is shown in Fig. 3D. The peak potential remained constant at pH values below 6, but was shifted towards more negative potentials when the pH was increased, at a rate of ~ 70 mV/pH unit, as a result of enhanced stability of the vanadium complex at higher pH values. A pH value of 6.6 (obtained by addition of $200 \mu\text{l}$ of 1 M PIPES buffer to sea water sample) was selected for the optimised analytical conditions to determine vanadium in sea water.

3.4. Effect of varying voltammetric parameters: square-wave frequency, deposition potential and deposition time

The sensitivity of CSV is affected by the deposition potential as it determines the charge on the electrode and therefore the Coulombic attraction or repulsion. The CSV sensitivity was recorded as a function of the deposition potential using a constant deposition period (15 s) and each scan was carried out from -0.4 V to -1.2 V using the square-wave modulation (50 Hz). The effect of the deposition potential on the peak height is shown in Fig. 4A. It was found that the peak

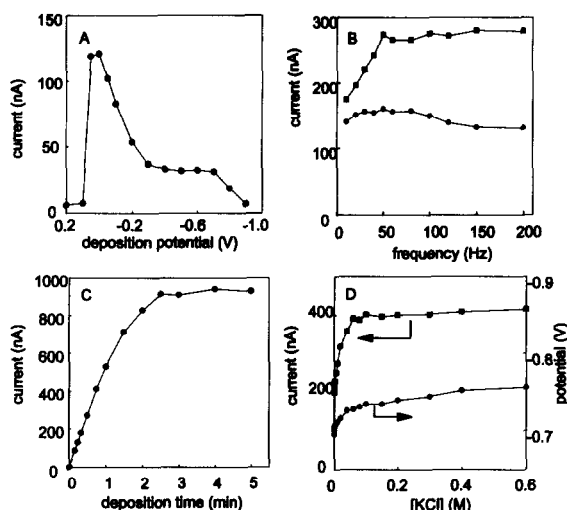


Fig. 4. Effect of varying voltammetric parameters and the concentration of chloride on the sensitivity for 20 nM vanadium in UV-digested purified sea water (A,B and C) and PIPES buffer solution (D). (A) Variation of the deposition potential using a deposition period of 15 s. (B) Variation of the square-wave frequency after a deposition period of 20 s (●) and 60 s (■). (C) Variation of the deposition period. (D) Variation of the chloride concentration on the current (■) and potential (●) of the CSV peak after a deposition period of 60 s for 20 nM vanadium in 20 mM PIPES buffer.

current was almost zero at positive values of the deposition potential presumably due to oxidation of the mercury surface. Highest sensitivity was obtained at a deposition potential between 0.0 and -0.1 V, decreasing at more negative values and remaining constant at potentials more negative than -0.3 V. The apparently favourable adsorption conditions at potentials where the mercury electrode has a positive surface charge suggest that the catechol–vanadium complex has a negative charge.

The effect of varying the square-wave frequency on the CSV peak height for 20 nM vanadium in sea water is shown in Fig. 4B. Scans were performed after either 20 or 60 s deposition at -0.1 V. The peak current increased with increasing frequency levelling off at frequencies above 50 Hz. Higher frequencies led to faster scans, but without improvement of the signal/noise ratio probably due to slow kinetics of the catalytic

redox couple. A frequency of 50 Hz was used in subsequent experiments.

Variation of the deposition time showed that the peak height increased linearly with the deposition time, gradually levelling off at periods longer than 2 min (Fig. 4C) presumably due to saturation of the mercury surface with catechol complexes with vanadium and other elements. A deposition time of 15 s is adequate for the determination of vanadium in sea water because of the high sensitivity of the catalytic current. The data in Fig. 4C show that the sensitivity can be increased by a factor of eight by extending the adsorption period to 2 min.

Comparative determinations of the CSV sensitivity for vanadium in water (Milli-Q) and sea water showed that the sensitivity was greater in sea water. Variation of the concentration of chloride in water (Fig. 4D) showed that the CSV peak height approximately doubled when the chloride concentration was increased to 0.1 M, whilst the increase levelled off at higher chloride concentrations. A concomitant shift of the peak potential with increasing chloride concentration (Fig. 4D) suggests that the adsorbed complex is stabilised in this condition, possibly caused by the formation of a mixed (vanadium–catechol–chloride) complex with better adsorptive properties.

3.5. Interferences

Species such as Al(III), As(III), Cd(II), Co(II), Cr(VI), Cu(II), Fe(III), In(III), Mn(II), Mo(VI), Ni(II), Sb(III), Se(IV), Ti(IV), U(VI) and Zn(II) are able to form complexes with catechol [18,19] and are therefore potential interferences in the determination of vanadium. The selectivity of the optimised method was tested by addition of 100 nM of these metals to sea water containing 30 nM vanadium(V) in the presence of 20 mM potassium bromate and 0.2 mM catechol, using a deposition time of 15 s. In these conditions, small additional peaks were observed for Cu (–0.19 V, sensitivity (S) = 0.86 nA/nM), Fe(III) (–0.35 V, S = 0.61 nA/nM), Mo (VI) (–0.45 V, S = 0.10 nA/nM), Pb (–0.41 V, S = 0.34 nA/nM) and U(VI) (–0.53 V, S = 0.04 nA/nM) which were not found to interfere with the determination of

vanadium (S = 9.6 nA/nM). High levels (100 nM, S = 1.36 nA/nM) of indium did interfere yielding a overlapping peak and decreasing the height of the vanadium peak. However, this interference does not occur in sea water as the indium concentration in sea water is very low (pM level).

Surface-active organic matter occurring in natural waters can interfere as a result of competitive adsorption on the mercury surface. Several surface-active substances, dodecylbenzenesulphonic acid (sodium salt, DBS, an anionic surfactant), Hyamine 1622 (a cationic surfactant) and Triton X-100 (a non-ionic surfactant) were used as model compounds for natural organic surfactants in sea water. These compounds were found to interfere less than usual in CSV, probably due to the short deposition time (15 s) used for the determination of vanadium in sea water. The peak of 30 nM vanadium in UV-digested sea water was diminished by ~ 50% in the presence of 2.6 ppm ($\mu\text{g ml}^{-1}$) Hyamine 1622, 5.2 ppm DBS and 3.2 ppm Triton X-100. The vanadium peak was completely masked in the presence of 5 ppm Hyamine, 10 ppm DBS or 5 ppm Triton X-100. It is likely that such substances affect the sensitivity when vanadium is determined in natural water samples. For instance the CSV sensitivity for vanadium in Mediterranean sea water was 8% less than that after UV digestion of the sample at pH 2. It is therefore advisable to calibrate the sensitivity for each sample separately by means of a vanadium standard addition to the sample. However, the same concentration is obtained before and after the UV digestion at pH 2, so this treatment is necessary only if the sensitivity is greatly diminished as in samples containing high levels of organic surface-active substances. Comparative measurements indicated that vanadium could be readily determined in sea water from estuarine or coastal origin.

3.6. UV digestion of sea water to remove interfering organic matter

UV digestion can be used to remove interfering organic matter with complexing or surface active properties. Preliminary experiments comparing UV digestion of acidified (to pH 2 with

hydrochloric acid) and unacidified sample aliquots (filtered Mediterranean sea water) and with and without addition of a known amount of vanadium standard indicated losses of 20–30% of vanadium from unacidified aliquots (Table 1). Furthermore, the vanadium concentration in the unacidified aliquots was found to decrease with increasing storage time suggesting that the vanadium adsorbed on the silica tube or on inorganic particles formed during the UV digestion at neutral pH.

Curiously, the CSV sensitivity for vanadium was not stable in acidified UV-digested samples, as the peak for vanadium increased with subsequent scans. Previously it has been shown that hypochlorite is formed upon UV digestion of acidified sea water interfering with the subsequent determination of copper [20]. Additions of hypochlorite confirmed that this has an interfering effect on the CSV peak for vanadium, confirming that the hypochlorite formation was the cause of the interference observed in UV-digested sample aliquots. This interference was eliminated by addition of 0.2 mM hydroxylammonium chloride to the sea water sample buffered at pH 6.6 to reduce the hypochlorite, and then bubbling nitrogen through the sample for 3 min prior the addition of bromate and catechol.

3.7. Linear range, sensitivity and limit of detection

The linear calibration range of the optimised method was evaluated from a calibration plot of vanadium in purified (by ion exchange to lower

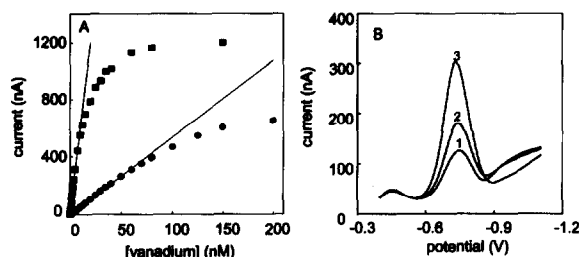


Fig. 5. CSV (square-wave modulation, 50 Hz) of vanadium in purified and UV-digested sea water. (A) Response as a function of the vanadium concentration after 15 (●) and 120 (■) s deposition at -0.1 V. (B) CSV scans of low levels of vanadium using a deposition time of 5 min; vanadium concentrations: 1, 0.35 nM; 2, 0.6 nM; 3, 1.35 nM.

the vanadium concentration) and UV-digested sea water (to remove potentially interfering organic substances). Calibration graphs are shown for two deposition times in Fig. 5A, whilst low vanadium level (0.35 to 1.35 nM, much lower than normally occurring in sea water) scans are shown in Fig. 5B. The peak current was found to increase linearly with the vanadium concentration between 0.2 and 10 nM when a 120 s deposition period was used, whereas the linear range was from 2 to 60 nM using a 15 s deposition period.

The sensitivity of the method (calculated from the slope of a linear regression) was 60 nA nM^{-1} for the 120 s deposition period and 5.4 nA nM^{-1} for the 15 s deposition period.

The 3σ limit of detection was calculated from repeated CSV determinations of a low level (1 nM) of vanadium in purified sea water. The limit of detection was 0.07 nM (R.S.D. 2.2%) using a deposition time of 120 s, whereas it was 0.6 nM (R.S.D. 19%) using a deposition time of 15 s.

4. Conclusions

The reduction current of vanadium in an adsorbed complex with catechol (possibly a mixed complex with chloride when the analysis is carried out on sea water) is catalytically enhanced in the presence of bromate. The catechol is added in oxidised form (orthobenzoquinone) to the solution premixed with the bromate. The deposition step is complicated, involving the electrolytic re-

Table 1

Influence of UV digestion on the concentrations of vanadium in sea water originating from the Mediterranean detected by CSV after a deposition time of 15 s (n indicates the number of repeats)

Sample pretreatment	Detected vanadium (nM)	R.S.D. (%)
Untreated	24.9 ± 1.5 ($n = 5$)	6.0
UV-digested at pH 8	20.2 ± 4.4 ($n = 8$)	21.8
UV-digested at pH 2	25.1 ± 1.3 ($n = 5$)	5.2
+ 20 nM vanadium		
Untreated	46.9 ± 2.0 ($n = 5$)	4.3
UV-irradiated at pH 8	33.5 ± 0.6 ($n = 4$)	1.8
UV-irradiated at pH 2	47.7 ± 3.7 ($n = 4$)	7.8

duction of the orthobenzoquinone back to catechol at -0.1 V with subsequent complex formation with vanadium(V) and adsorption on the mercury electrode. The vanadium in the adsorbed complex is reduced to vanadium(IV), and is reoxidised to vanadium(V) in the diffusion layer by the dissolved bromate, and is available for re-reduction thus catalytically enhancing the reduction current. The limit of detection is 0.6 nM using a deposition time of 15 s, so vanadium can be determined in sea water very quickly. Potential interference by surface-active organic compounds is comparatively minor because of the short deposition period used, so UV digestion is normally not required. However, if used, UV digestion has to be carried out after acidification of the sample, and any hypochlorite resulting from the UV digestion in saline waters has to be removed using hydroxylammonium chloride prior to the analysis.

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