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# Direct Electrochemical Determination of Dissolved Vanadium in Seawater by Cathodic Stripping Voltammetry with the Hanging Mercury Drop Electrode

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**Polarographic measurements showed that catechol complexes of vanadium(V) adsorb onto the hanging mercury drop electrode. This property forms the basis of a sensitive electrochemical technique by which dissolved vanadium in seawater can be determined directly. The reduction current of adsorbed complex ions of vanadium is measured by differential pulse cathodic stripping voltammetry, preceded by a period of collection of a few minutes. The peak potential is at  $\sim -0.7$  V. Optimal experimental parameters were found to be a catechol concentration of  $2 \times 10^{-4}$  M, a collection potential of  $-0.1$  V, and a solution pH of 6.9. The limit of detection is 0.3 nM vanadium after a 2-min collection with a stirred solution, which is decreased further to 0.1 nM after a 15-min collection.**

The concentration of dissolved vanadium in seawater lies in the range of  $(2-3) \times 10^{-8}$  M (1, 2). The predominant oxidation state is vanadium(V) (3), which at neutral pH occurs as the  $\text{VO}_2(\text{OH})_2^-$  ion, a hydrolysis product of  $\text{VO}_2^+$  (4). Its concentration is normally determined spectrophotometrically after some form of preconcentration by means of coprecipitation, solvent extraction, or adsorption on a cation exchange resin (2, 5, 6). After preconcentration the element can also be determined polarographically by using a dropping mercury electrode (DME) in solutions containing 1 M ammonia (7). The reduction potential of vanadium(V) lies at  $-1.07$  V (vs. SCE) in those conditions, whereas in noncomplexing electrolytes the reduction wave is masked by discharge of mercury as its half-wave potential is at  $+0.76$  V. Concentrations of vanadium between  $10^{-7}$  and  $10^{-5}$  M can also be determined by cathodic stripping voltammetry (CSV) after a collection step which involves the formation of the  $\text{Hg(I)}$  salt of the anion at  $+0.4$  V on a hanging mercury drop electrode (HMDE) (8). None of these techniques is sufficiently sensitive to determine vanadium directly in seawater. It was therefore found useful to develop a more sensitive electrochemical technique.

It has been shown recently that certain metal ions can be made to adsorb onto a HMDE as a result of the formation of surface active complexes. Thus, low concentrations of for instance Ni (9), Cu (10), and U (11) can be determined in seawater in the presence of dimethylglyoxime (9) or catechol (10, 11). Preliminary experiments were performed with various complexing ligands in order to investigate their use for the determination of vanadium. Greatest sensitivity was obtained with catechol. The results of a detailed study into the optimal analytical conditions for the determination of vanadium using this ligand are therefore reported in this paper.

## EXPERIMENTAL SECTION

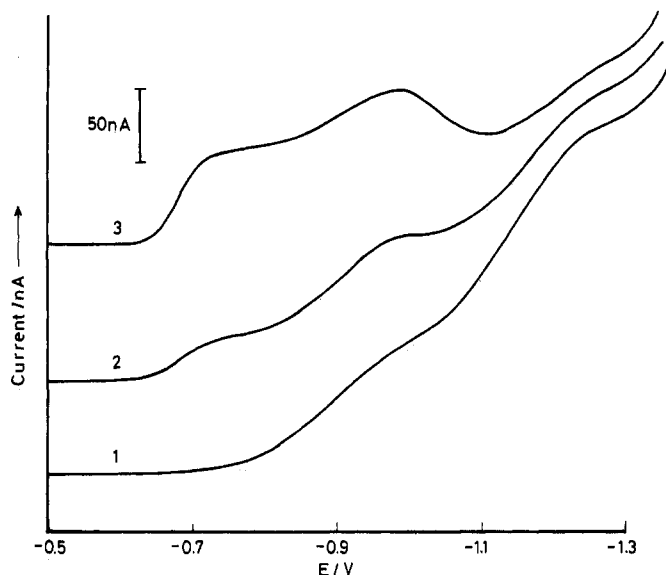
Equipment and chemicals were the same as before (10, 11). The surface area of the HMDE was  $2.92 \text{ mm}^2$ . Potentials are quoted relative to the  $\text{Ag/AgCl}$  reference electrode unless indicated

differently. A stock aqueous solution of vanadium (V) was prepared by dilution of BDH standard solution for atomic absorption spectroscopy. A stock solution of 0.1 M catechol in deaerated distilled water was prepared freshly every day. A pH buffer solution of 1 M PIPES (piperazine- $N,N'$ -bis(2-ethanesulfonic acid)) was prepared by dissolution of its monosodium salt in 0.5  $\text{NH}_4\text{OH}$ . Seawater collected from the surface of the Atlantic ocean was stored frozen. The sample was analyzed either by direct methods or after UV irradiation for 3 h by a 1-kW lamp, as indicated in the text.

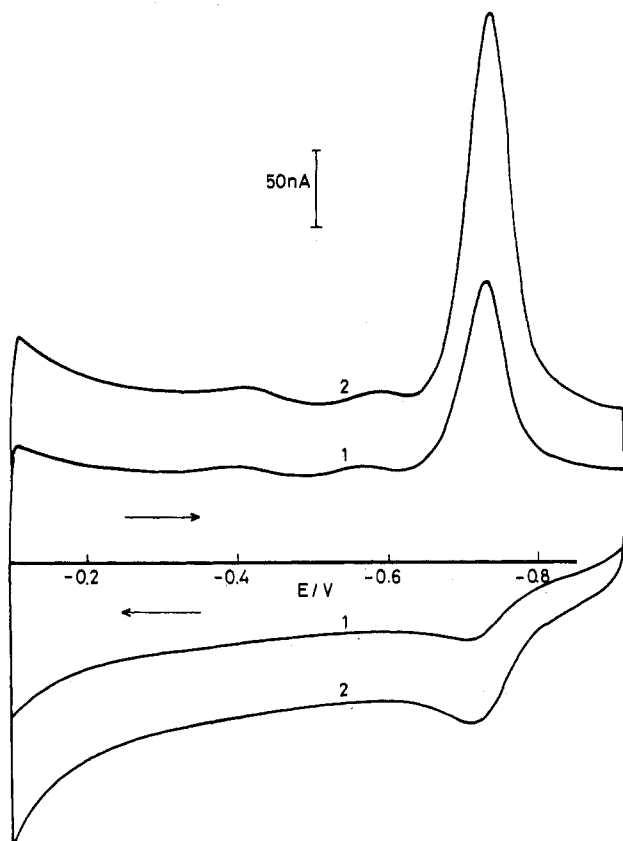
**Procedure.** Of the sample 10 mL is pipetted into the polarographic cell. The pH is adjusted to 6.9 by the addition of 100  $\mu\text{L}$  of 1 M PIPES pH buffer, the solution is deaerated by purging with Ar gas, and 20  $\mu\text{L}$  of 0.1 M catechol (final concentration  $2 \times 10^{-4}$  M) is pipetted into the solution. A new mercury drop is extruded, the potential of the HMDE is set to  $-0.1$  V, and the stirrer is started which signifies the beginning of the collection period. The length of the period of preconcentration depends on the expected vanadium concentration, but 1 min was found to be sufficient for seawater of 35‰ salinity. The CSV scan is started 15 s after stopping of the stirrer. The differential pulse modulation is applied, using a pulse rate of 10/s and a scan rate of 10 mV/s (a slower pulse rate or use of the linear sweep potential scan causes the sensitivity to diminish; for instance, the peak height is  $\sim 25\%$  less at a pulse rate of 2/s and a scan rate of 5 mV/s). The procedure is repeated after a standard addition of  $2 \times 10^{-8}$  M vanadium(V). The increase of the peak current as a function of the vanadium concentration is linear until  $\sim 10^{-7}$  M if a collection period of 1 min is used. It is recommended to UV-irradiate the sample if the presence of organic surfactants is suspected (in coastal seawater for instance). Thus, the peak height is diminished by 60% by 1 mg/L of surfactants similar to Triton-X-100.

## RESULTS AND DISCUSSION

**Dc Polarography and Cyclic Voltammetry.** Measurements using sampled dc polarography with a DME revealed that the reduction wave of  $2 \times 10^{-5}$  M V(V) in seawater, buffered at pH 6.9 by 0.01 M PIPES, appears at  $-0.90$  V, followed by the reduction wave of V(IV) to V(II) (7) at  $\sim -1.2$  V (see Figure 1, scan 1). The wave at  $-0.90$  V is due to the hydrolyzed ion of V(V) (7). Another wave, having a half-wave potential,  $E_{1/2}$ , of  $-0.67$  V, appeared when  $10^{-4}$  M catechol was added to the solution (Figure 1, scan 2). An increase in the catechol concentration to  $4 \times 10^{-4}$  M caused the wave at  $-0.67$  V to reach the height of the wave at  $-0.90$  V (as a result of complexation of all dissolved vanadium by catechol), and an adsorption maximum appeared at  $\sim -0.97$  V (Figure 1, scan 3). The wave at  $-0.67$  V represents the reduction of the catechol complex with V(V): which is apparently reduced more easily than the hydrolyzed ion (this wave was not shifted to this potential as a result of possible complexation of V(IV) by catechol because the reduction potential of the third wave at  $-1.2$  V was unaltered). A plot of  $\log(i/(i_d - i))$  as function of  $E$  for the wave at  $-0.67$  V (in presence of  $4 \times 10^{-4}$  M catechol) was straight and had a slope $^{-1}$  of 33 mV (apparent  $n = 1.7$ ). A similarly steep reduction wave has been observed

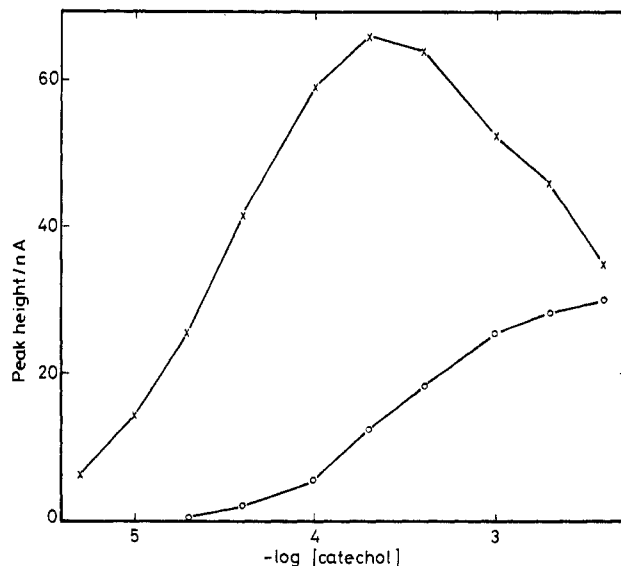


**Figure 1.** Dc polarography using a DME of  $2 \times 10^{-5}$  M vanadium in seawater of pH 6.9, in the presence and absence of catechol. Scan rate 2 mV/s, drop rate 2/s. Scans: 1, pH 6.9; 2, addition of  $10^{-4}$  M catechol; 3,  $4 \times 10^{-4}$  M catechol.



**Figure 2.** Cyclic voltammetry with a HMDE of  $3.8 \times 10^{-7}$  M vanadium in seawater of pH 6.9 and containing  $2 \times 10^{-4}$  M catechol, after a 1-min stirred collection at  $-0.1$  V. Scans: 1, scan rate of 50 mV/s; 2, 100 mV/s.

before for complexes of Cu(II) with catechol (10). The reversibility of the reduction of the V(V)-catechol complex was estimated by cyclic voltammetry, using a HMDE, as shown in Figure 2. The cathodic current was much greater than the anodic, indicating that only the V(V) complex ion adsorbs. The cathodic peak potential shifted 10 mV in the negative direction when the sweep rate was increased from 50 to 200 mV/s; this shift is smaller than the corresponding shift of 42 mV for catechol complexes of Cu(II) (10). The anodic peak potential was  $\sim 30$  mV more positive than the cathodic peak



**Figure 3.** Effect of catechol concentration on LSCSV peak heights in seawater containing  $7 \times 10^{-8}$  M vanadium. Scans were performed after a 1-min collection at  $-0.1$  V, using a scan rate of 50 mV/s. (X) First peak at  $-0.73$  V; (O) second peak at  $-0.80$  V.

potential (at both sweep rates) as a result of diffusion of V(IV) away from the surface of the HMDE. This potential difference is only about 10% of the corresponding difference for catechol complexes with U(VI) (11) as the reduction of complexed vanadium is apparently more reversible.

**Effect of Variation of the Catechol Concentration.** The optimal catechol concentration for analytical purposes was determined by linear sweep (LS) CSV of seawater (containing  $7 \times 10^{-8}$  M vanadium), at a fixed pH of 6.9 (in presence of 0.008 M PIPES buffer). It was found (see Figure 3) that the greatest peak height was obtained at a catechol concentration of  $2 \times 10^{-4}$  M. At catechol concentrations greater than  $\sim 2 \times 10^{-5}$  M a second, much smaller peak appeared at a more negative potential than the first. The height of this second peak continued to increase until it was almost the same size as the first peak at a catechol concentration of  $4 \times 10^{-3}$  M. The peak potential of the first, main peak did not change with variation in the catechol concentration and was located at  $-0.73$  V, whereas the potential of the second peak was at  $-0.80$  V in  $10^{-4}$  M catechol and at  $-0.77$  V in  $2 \times 10^{-3}$  M catechol. The second peak was much smaller than the first at the optimal catechol concentration of  $2 \times 10^{-4}$  M and was so near to the main peak that it was normally masked when the differential pulse modulation (with a pulse height of 25 mV) was used. Greatest peak height of the main peak was obtained at catechol concentrations between 1 and  $2.5 \times 10^{-4}$  M. The following experiments were therefore carried out with seawater containing  $2 \times 10^{-4}$  M catechol.

**Effect of Variation of the pH.** The effect of the solution pH on the adsorption of complexes of vanadium with catechol onto the HMDE was determined by DPCSV measurements after a collection time of 1 min, at a potential of  $-0.1$  V. The scan was performed by using a scan rate of 5 mV/s, a pulse rate of 2/s, and a pulse modulation of 25 mV. It was found (Figure 4) that maximum adsorption was attained at  $\sim$  pH 6.9, whereas at higher pH values the adsorption diminished again probably as a result of competitive hydrolysis of the  $\text{VO}_2^+$  ions. The peak potential was found to shift in a negative direction which reflects the increased stability of complexes with catechol at higher pH values. A pH value of  $\sim 6.9$  was selected for the determination of the vanadium concentration in seawater, as the peak height is greatest at this pH and because the solution pH can be readily buffered at this value with PIPES buffer.

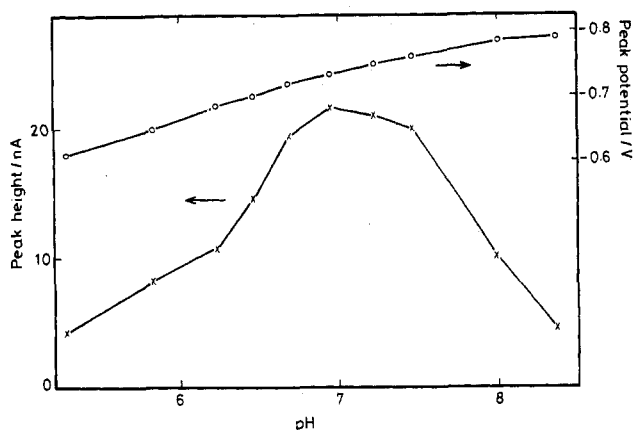


Figure 4. Effect of pH on the DPCSV peak height and potential of  $4 \times 10^{-8}$  M vanadium in seawater. (X) Peak height; (O) peak potential.

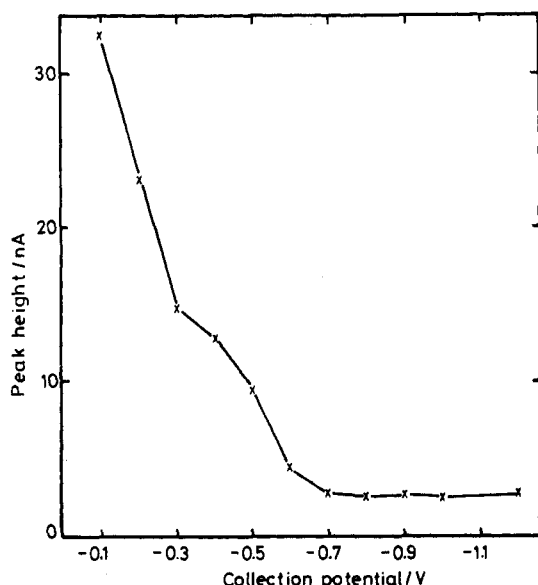


Figure 5. Effect of collection potential on the DPCSV peak height of  $7 \times 10^{-8}$  M vanadium in seawater.

**Effect of Variation of the Potential and Period of Collection.** Measurements of the reduction current of adsorbed V(V)-catechol complexes were performed by DPCSV after a collection time of 1 min at selected potentials. Each scan was started at  $-0.5$  V by using a scan rate of  $5$  mV/s and a pulse rate of  $2$ /s. The electrocapillary maximum (ECM) of mercury in a chloride solution similar to seawater is at  $\sim -0.52$  V (12). It was found (Figure 5) that the reduction current was greatest after collection at the most positive potential of  $-0.1$  V and decreased with selection of more negative collection potentials (nearer the ECM) until a small constant peak current had been reached at  $-0.7$  V. This effect is due to the negative ionic charge of the complex ions of V(V) with catechol. It is also evident that reduced vanadium ions (V(IV)) do not adsorb onto the HMDE, as the residual current could be explained by adsorption of V(V) complex ions during the 60-s period between switching to  $-0.5$  V and scanning until the reduction potential of vanadium (at  $-0.73$  V) had been reached.

Measurements of the reduction current as a function of the collection time at a fixed collection potential ( $-0.1$  V) are reported in Figure 6. The current was measured by LSCSV by using a scan rate of  $50$  mV/s. It was found that the increase in the peak current with the collection period was linear up to only about 3 min at low concentrations ( $<4 \times 10^{-8}$  M) of vanadium and up to about 1 min in the presence of  $10^{-7}$  M vanadium where a maximum of  $210$  nA was reached after a

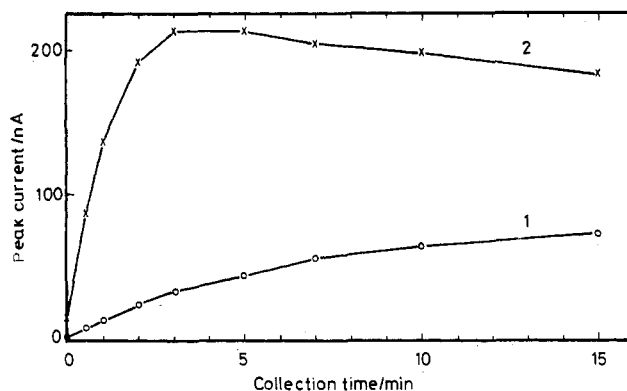


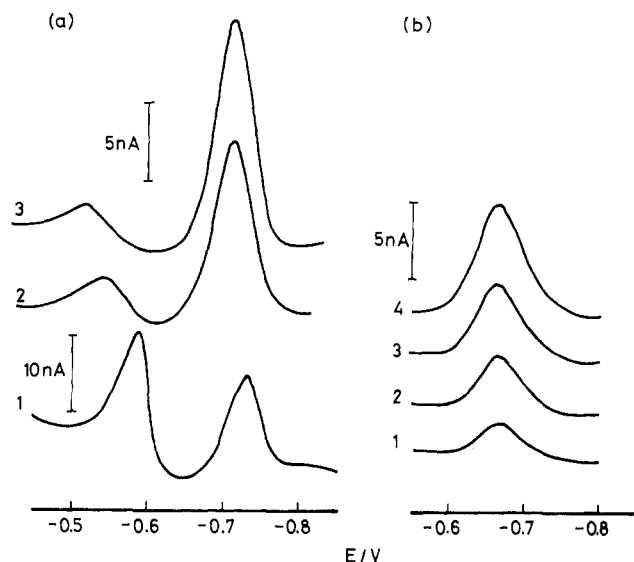
Figure 6. Effect of collection time on the LSCSV peak height of  $4 \times 10^{-8}$  M (curve 1) and  $1.2 \times 10^{-7}$  M vanadium (curve 2), in seawater.

period of 3 min. Higher currents, up to  $330$  nA after a collection period of 1 min, could be obtained at enhanced vanadium concentrations. The present maximum current of  $210$  nA was less because of competitive adsorption of complexes of traces of copper and uranium which apparently occupy about 30% of the surface of the HMDE after a collection period of 3 min.

**Maximum Adsorption Density of Vanadium.** The maximum adsorption density of catechol complexes of vanadium was calculated from LSCSV measurements of the reduction current as a function of the dissolved vanadium concentration, after a fixed adsorption period of 1 min. The total charge (in Coulombs) passing through the HMDE was determined by measuring the surface area under the peak. The data were then fitted to a modified version of the Langmuir equation (10). This experiment was repeated at three collection potentials ( $-0.1$ ,  $-0.3$ , and  $-0.5$  V) in order to investigate its effect on the adsorption density. The maximum density was represented by a charge of  $0.77 \mu\text{C}$  after collection at both  $-0.1$  and  $-0.3$  V and  $0.72 \mu\text{C}$  after collection at  $-0.5$  V. This density ( $0.77 \mu\text{C}$  being equivalent to an adsorbed layer of  $2.7 \times 10^{-10}$  mol/cm<sup>2</sup>) is similar to that found previously for copper (10). Each adsorbed complex ion of vanadium thus occupies in area of  $0.61$  nm<sup>2</sup> in conditions of surface saturation, which may be compared with the calculated surface area of  $0.68$  nm<sup>2</sup> which would be covered by a molecule of the type VL<sub>2</sub> (L being catechol) if adsorbed flat onto the mercury surface (13). Speciation of V(V) with catechol in solution could not be calculated as no values for stability constants for such complexes were available to the authors.

**Interferences.** The capacity of a number of metals (such as Pb, U, Sb, Zn, Cd, Fe, and Bi) to form reducible complexes with catechol and adsorb onto the HMDE was tested by standard addition of these metals. It was found that the vanadium peak is preceded by that of uranium and followed by that of antimony. The sensitivity toward antimony is low, and no peak is visible in unpolluted seawater at the stated conditions. A peak is present for uranium (11), but this peak is about  $0.18$  V more positive than that of vanadium and was not found to interfere with the estimation of the peak height of vanadium at the usual uranium concentration ( $1.3 \times 10^{-8}$  M) in seawater of 35‰.

However, it was found that natural organic surfactants present in seawater from the coastal origin (Irish Sea) reduced the peak height of vanadium considerably: the peak height for a given vanadium concentration in seawater which had been stored for a prolonged period was found to be reduced by about 70% compared with a UV-irradiated aliquot of the sample. The nonionic surfactant Triton X-100 has been used before as a model for natural organic surfactants in seawater (14). It was then found that suppression of the capacitance on a HMDE by surfactants present in coastal seawater was

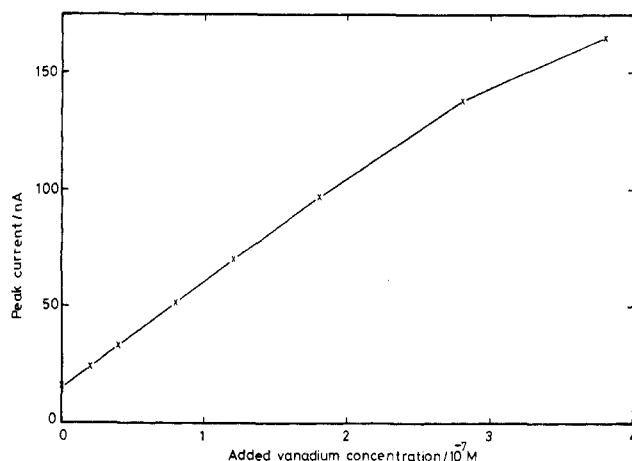


**Figure 7.** Determination of vanadium in seawater (a) and in 0.01 M KCl (b). (a) Collection time of 1 min. Scans: 1, LSCSV, scan rate 50 mV/s; 2, DPCSV, scan rate 5 mV/s, pulse rate 2/s; 3, DPCSV, scan rate 1/ mV/s, pulse rate 10/s. (b) Collection time of 2 min and using DPCSV, scan rate 1/ mV/s, pulse rate 10/s. Scans: 1,  $3 \times 10^{-9}$  M vanadium; 2,  $5 \times 10^{-9}$  M; 3,  $7 \times 10^{-9}$  M; 4,  $11 \times 10^{-9}$  M.

similar to that caused by 0.01–0.5 mg/L of Triton. Measurements of vanadium in UV-irradiated seawater before and after additions of Triton revealed that the peak height was reduced by 12% by 0.5 mg/L of Triton, 60% by 1 mg/L, and completely disappeared in the presence of 2 mg/L. It was therefore normally found to be necessary to treat samples from coastal origin with UV irradiation. A large fraction of the dissolved uranium concentration is conveniently removed by the same treatment (11).

**Determination of Vanadium in Seawater and in 0.01 M KCl.** A catechol concentration of  $2 \times 10^{-4}$  M was selected to determine the dissolved vanadium concentration in surface seawater from the Atlantic (10) and in an electrolyte solution of 0.01 M KCl. The solutions was buffered at pH 6.9 with 0.01 M PIPES. The measurements in seawater were performed after a collection period (with stirred solution) of only 1 min at a potential of  $-0.1$  V (Figure 7a). The reduction current was recorded by LSCSV (scan 1) by using a scan rate of 50 mV/s and by DPCSV by using either a pulse rate of 2/s with a scan rate of 5 mV/s (scan 2) or a pulse rate of 10/s with a scan rate of 10 mV/s (scan 3). The peak at  $-0.59$  V (scan 1) was caused by a trace amount ( $5 \times 10^{-9}$  M) of uranium, while the vanadium peak was apparent at  $-0.73$  V. The height of the vanadium peak was much increased relative to that of uranium when the differential pulse modulation was used, and also the peak potentials are further apart (0.19 V as opposed to 0.14 V when LSCSV was used) as a result of the greater reversibility of the reduction of adsorbed complexes of vanadium. Variation of the pulse and scan rates showed that the peak height of vanadium increased by  $\sim 13\%$  when, instead of a pulse rate of 2/s and a scan rate of 5 mV/s, a pulse rate of 5/s and a scan rate of 10 mV/s were used; the peak height increased by a further 12% when a pulse rate of 10/s (scan rate 10 mV/s) was used and again by 27% when the scan rate was increased to 20 mV/s (pulse rate 10/s). It was found, however, that the resolution was less at a scan rate of 20 mV/s.

A pulse rate of 10/s and a scan rate of 10 mV/s (other conditions being the same) were selected for the determination of the vanadium concentration in the seawater sample by means of standard additions. It was evident that the increase in the peak height with the metal concentration was linear



**Figure 8.** Peak height as a function of the vanadium concentration in seawater, measured by DPCSV (10 mV/s, 10 pulses/s) after a 1-min collection; Initial vanadium concentration in the sample was about  $3 \times 10^{-8}$  M.

until a total vanadium concentration of about  $2 \times 10^{-7}$  M (Figure 8), whereafter the sensitivity diminished as a result of saturation of the surface of the HMDE. The sample was found to contain  $3.2 \times 10^{-8}$  M vanadium which agrees well with reported values (1, 2). The relative standard deviation of the determination of this metal concentration was found to be  $\pm 2.3\%$  (8 degrees of freedom). The same experimental conditions (after a collection period of 2 min) were used for the analysis of 0.01 M KCl to which  $3 \times 10^{-9}$  M vanadium had been added (Figure 7b). The measurement was repeated after standard additions of 2 (scan 2), 4 (scan 3), and  $8 \times 10^{-9}$  M (scan 4) of vanadium. The relative standard deviation for the determination of  $3 \times 10^{-9}$  M vanadium was found to be 3.6% (10 degrees of freedom), from which a detection limit ( $3\sigma$ ) of  $3 \times 10^{-10}$  M can be calculated (15). This detection limit can be reduced further by increasing the collection time until a limit of  $\sim 1 \times 10^{-10}$  M is obtained after a collection time of 15 min.

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**Registry No.** Vanadium, 7440-62-2; water, 7732-18-5.

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