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VOLTAMMETRIC DETERMINATION OF VANADIUM WITH ADSORPTIVE PRECONCENTRATION OF THE PYROCATECHOL VIOLET COMPLEX

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Summary—A sensitive stripping voltammetric procedure for trace measurements of vanadium in aqueous samples is reported The method is based on the interfacial accumulation of the vanadium–pyrocatechol complex onto the hanging mercury drop electrode, followed by reduction of the adsorbed complex The limit of detection is 0.1n*M* vanadium after a 3 min collection with a stirred solution at pH 4 7 The procedure is selective with respect to other metals and has been applied in analyzing various samples

Vanadium is present in materials of environmental interest usually at very low concentrations. The average crustal abundance is in the range 100–150 μg/g, sea-water and contains between 20 and 60n*M* V while the level in fresh water has been found to range from 4 to 4000n*M*. These values, as well as concentrations in other environmental matrixes, have been documented in a review.[1] One of the major anthropogenic releases of V to the environment is through the combustion of oil and coal. Background air concentrations are 0.2–1.9 ng/m^3 but urban air, where high V fuel is used, averages about 500 ng/m^3.

The determination of V in environmental samples presents a considerable challenge in terms of sensitivity in the presence of much higher concentrations of potentially interfering elements. Many techniques have been recommended for this analysis, and each has its own advantages and limitations.

Atomic spectroscopy methods are widely used with electrothermal atomization atomic absorption often being recommended for trace V analysis. However, the refractory nature of the element leads to difficulties in atomization with resulting poor sensitivity.[2–5] Using the inductively coupled plasma as an emission source, more efficient atomization and excitation is possible, yet separation and preconcentration may be required for analysis of such materials as natural waters,[6] silicate rocks and coal fly ash,[7] and iron metal.[8] Inductively coupled plasma-mass spectrometry is still more sensitive,[9] but the fact that V is naturally monoisotopic poses difficulties in terms of calibration as the use of the isotope dilution technique is obviated.

Spectrophotometric methods generally lack the selectivity and sensitivity required in trace analysis. In spite of this, with mixed success a wide variety of ligands have been used to complex V and produce species having large molar absorptivities. Some commonly-used ligands include: pyrogallol,[10] PAR,[11] catechol violet,[12] pyrocatechol violet,[13] pyridylazophenol,[14] 1,10-phenanthroline,[15] glycinecresol red[16] and 3-hydroxyflavone.[17] Recent attention has focused on utilization of ternary complexes or ion-associated compound involving V, a chromophoric ligand and a third agent which enhances the spectrophotometric sensitivity of the complex. By the use of surface-active agents, especially those of the pyridinium and trimethyl ammonium series, it has been possible to vary the protolytic complex-forming properties, solubility, and ability to be extracted, and thus to considerably increase the efficiency of utilization of organic ligands in analysis. The spectrophotometric procedures have been recommended for analysis of V in steel, soils, fuel oil, soil, waste water, biological material, etc.

A current trend in analysis of V is employment of the well-known catalytic effect of BrO_3^- and ClO_3^- to enhance sensitivity of the spectrophotometric methods. The catalytic pro-

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cedures depend on the ability of V to increase the rate of certain reactions whose products are detected spectrophotometrically. The detection limits of the catalytic methods are reported to be at nM level[18] and in a few cases even at the pM level [19]

In order to determine ultratrace concentrations of V, a separation and preconcentration technique is frequently required Many such preconcentration techniques have been proposed, including extraction, precipitation, coprecipitation and ion exchange. These techniques have been used prior to various instrumental methods of analysis. Reversed phase HPLC[20] and ion chromatography[21] are also used for ultra trace analysis. Other techniques occasionally recommended for V analysis include: NAA,[22] XRF,[23] PIXE,[24] fluorometry[25] and EPR (ESR).[26]

Electrochemical methods for V analysis have not generally been developed as extensively as the spectrochemical techniques. After preconcentration, V can be determined polarographically,[27] or by a coulometric titration method.[28] Vanadium can be determined also by cathodic stripping voltammetry (CSV) at concentrations between 0.1 and 10 μM [29] after a collection step which involves the deposition of the Hg(I) salt of the anion at +0.4 V on a hanging mercury drop electrode

Of the electroanalytical methods however, adsorptive stripping voltammetry (AdSV) may be the most sensitive for V analysis. In the usual form of AdSV, an excess of a ligand is used to convert the analyte to a complex species that can be adsorbed on the surface of a microelectrode. The adsorption is carried out in such a way that the rate of accumulation on the electrode is proportional to the concentration of the analyte species in the solution. The amount of adsorbed species is then measured by linear or differential pulse scan voltammetry, with a current peak for either oxidation or reduction of the coordinated ligand and/or the complex. The technique must be calibrated under conditions of use, usually by standard additions of the analyte. The method was first applied to the determination of Ni(II) using the DMG complex[30] and AdSV procedures have now been published for some 20 elements with detection limits in the pM to nM range.[31] The method has also been used for the detection of adsorbable organic species.[31]

Four AdSV methods have been described for V. In one,[32] catechol is used to complex the V(V) in order to determine dissolved V in sea-water. Adsorption on a Hg drop electrode at −0.1 V (*vs* SCE) and subsequent stripping with a differential pulse cathodic waveform gives a current peak at −0.7 V for reduction of the metal complex. The samples were buffered at pH 6.9 by 0.01M PIPES. The surface area of HMDE was 2.92 mm^2 and the estimated detection limit was 0.3nM V after a 2 min collection with stirred solution or about 0.1nM after 15 min collection. Qualitative data were reported concerning the possibility of interference of seven elements and it was indicated that some of these may produce overlapping peaks. There was no quantitative assessment of the extent to which this may be a problem of real analysis. Because natural organic surfactants seriously interfere with V analysis, UV irradiation for 3 hr using a 1-kW lamp was required. In the second method,[33] 2-(5′-bromo-2′-pyridylazo)-5-diethylaminophenol (5-Br–PADAP) was used as a ligand. The measurement was carried out at pH 4.5 in acetate buffered electrolyte. The metal complex was adsorbed on a Hg drop electrode at −0.24 V (*vs* SCE), and gave a current peak for reduction of the complex at −0.82 V. The detection limit, obtained by using linear scan stripping from a HMDE with surface area of 3.88 mm^2 after adsorption for an unspecified length of time was 0.5nM. Furthermore, the detection limit of 25pM was claimed by applying 1.5th and 2.5th order derivative adsorption voltammetry without specifying experimental conditions. The method was applied to tap-water analysis, with V content found to be in the range between 26 and 75nM. In spite of the fact that V concentrations in the samples were three orders of magnitudes above the reported detection limit, samples were preconcentrated prior to analysis. Experimental conditions as well as potential interferences were not specified. The method was also applied to samples of ore, and V content was found to be between 0.16 and 1.2μM.[34] It was reported that Co(II), Ni(II), Ti(IV), and $C_2O_4^{2-}$ may interfere; again experimental conditions were not reported.

In a recently-published method,[35] a detection limit in solution of 4.9pM V was reported. Cupferron was used as a complexing ligand and the presence of BrO_3^- enhanced sensitivity. The reduction peak potential for the V-cupferron complex was reported to be −0.09 V, *vs* an unspecified reference electrode. We found that the V–cupferron complex gives a reduction peak at −0.68 V against the Ag/AgCl/satd aq KCl

reference electrode. Although high selectivity with respect to other elements was claimed, the effect of Al was not studied and we have found that this element seriously interferes by giving reduction peak(s) at the same potential as V under the conditions specified for V analysis. The method was not tested by analyzing standard reference materials or other samples or by comparing with other techniques.

In the fourth method,[36] 2-(2′-thizolylazo)-*p*-cresol (TAC) was used as complexing agent. The detection limit of 3.9n*M* was achieved after preconcentration for 5 min on a large drop (0.032 cm^2) at 0.00 V (*vs* Ag/AgCl) in acetate buffer medium (pH 4.2) and stripping at a scan rate of 100 mV/sec The method was applied for analysis of a single sample of spring water which had a high level of V (1.9μM). Analysis was not very selective, seven ions would interfere if present at the same concentration level as V itself, six additional ions when in 10-fold excess and 23 cations and anions at a 100-fold excess.

We are presenting a fifth method which has advantages in terms of selectivity and may be used for trace V analysis in a variety of samples. The method uses pyrocatechol violet (PCV, 3,3′,4′–trihydroxyfuchsone–2″-sulfonic acid, H_4L) as a complexing agent. This ligand has previously been used in the AdSV determination of Al, and some of its chemical and electrochemical properties have been described in that study.[37]

EXPERIMENTAL

A Princeton Applied Research Corporation Model 174A Polarographic Analyzer was employed with a Model 303 Static Mercury Drop Electrode. The voltammograms were recorded using a Hewlett-Packard Model 7004A X-Y recorder and Bascon Turner Instruments recorder Model 3000. The three electrode system consisted of a 15 ml quartz cell with a static Hg electrode, a Pt auxiliary electrode and a Ag/AgCl/satd. aq KCl reference electrode separated from the analytical solution by a Vycor frit bridge. The electrolyte was stirred as required using a 0.9 cm Teflon "Spin Fin" driven at a rotation rate of 500 Hz. The usual AdSV experiment involved adsorption for 60 sec from stirred solution on a Hg drop (size "M", $A = 1.18$ mm^2) at −0.40 V. The stirring was turned off and after a 15 sec pause, the voltammetric measurement was made by scanning the electrode potential from −0.40 to −1.00 V at 0.05 V/sec.

The electrolytes were deaerated and blanketed throughout the experiment with CANOX "oxygen free" grade N_2 purified by passage over hot BASF catalyst (30% w/w Cu). The sample and cell manipulations were carried out in a laminar-flow clean hood with a high efficiency air filter. The glassware was cleaned by soaking in 3*M* aq HNO_3, and thoroughly rinsed.

The PCV was a reagent grade chemical supplied by BDH Chemicals. The ^1H NMR spectrum indicated a pure material. For AdSV, a stock 0.10m*M* PCV solution was prepared by dissolving a weighed amount of the reagent (pure material assumed) in distilled water. The solution was stable for periods exceeding 6 weeks.

The stock V(V) solution was prepared by dissolution of 0.900 g of V_2O_5 (99.5%) in hot conc HCl, addition of 10 ml conc HNO_3 and dilution to exactly 0.5 l with distilled water For analytical work a 20m*M* V standard was prepared by dilution of the stock solution with a pH 2.0 HNO_3 electrolyte.

The 0.5*M* acetate buffer solution was prepared by addition of aq NaOH to aq HOAc to give pH of 4.7. The buffer had been prepared from reagent grade chemicals

RESULTS AND DISCUSSION

Pyrocatechol violet

It is well-known that pyrocatechol violet (PCV), sometimes called catechol violet, forms stable complexes with a wide range of metallic elements. This property has led to its being called "the most promising reagent of the triphenylmethane series"[38]—a statement which refers to its potential as a ligand for use in spectrophotometric analysis. Much less has been reported with respect to its properties in electroanalytical studies. Our previous polarographic work[37] has shown that in acidic medium the ring carbonyl group of PCV is reduced in a single reversible two-electron step at a dropping mercury electrode with the half-wave potential dependent on the pH. In the case of Al, Cu, and Pb, when a complex is formed with the metal species, an additional reduction wave is generated at the expense of that due to the free ligand. The wave involves reduction of the complexed ligand, and it could also include a contribution due to reduction of the metal centre as well.

Species of vanadium in aqueous solutions

Thermodynamic calculations indicate that in simple aqueous solutions in equilibrium with the atmosphere at ambient temperatures, all solid and dissolved forms of V should be in the +5 oxidation state. The main soluble V inorganic species in well-aerated aqueous solutions like natural water under alkaline conditions are forms of the vanadate ion, VO_4^{3-}, with the degree of protonation depending on the solution pH.[39] Under highly acidic conditions (pH less than 2) the stable quinquevalent species is the VO_2^+ ion. It has been shown that in the intermediate pH range, various polymeric species are important, with a species containing 10 V atoms being a well-established example.[40]

While most environmental samples—water under aerobic conditions, and solid samples dissolved under oxidizing conditions—would be expected to contain forms of V(V), these species are moderately strong oxidizing agents and in the presence of organic matter or other reducing agents in oxygen-depleted water, could undergo reduction to give V(IV) species.

Most of the work reported here makes use of a standard solution of V(V) prepared as described above, however, almost identical results were obtained when using a V(IV) stock as long as the final analytical conditions were the same.

Electrochemistry of vanadium/pyrocatechol violet (V–PCV)

Direct current polarography of 0.10m*M* PCV spiked with concentrations of V from 0m*M* to 0.4m*M* in a 0.050*M* acetate medium gave two reduction waves with $E_{1/2}$ values of −0.53 V for PCV and −0.70 V for V-PCV. Increasing the V concentration resulted in a decrease in the first step and a growth of the second step, with the total limiting current near constant in all polarograms. Because the waves appear very close to one another it was not possible to accurately measure the relative sizes of two individual waves. The first wave results from the reduction of free PCV while the second results from the reduction of complexed PCV. Since it is known[37] that the reduction of PCV is a two electron process, it may be surmised that the same process (involving the ligand only) continues to take place in the complex. It appears that there is no remaining wave due to uncomplexed PCV after addition of an equimolar amount of V.

Direct voltammetry of 10μM PCV spiked with concentrations of V from 0.5μM to 10μM in a 0.125*M* acetate medium gave two reduction peaks at potentials of −0.60 V for PCV and −0.75 V for V–PCV. Sensitivity of 40 nAμM V makes the direct voltammetry method applicable in V analysis at μM level.

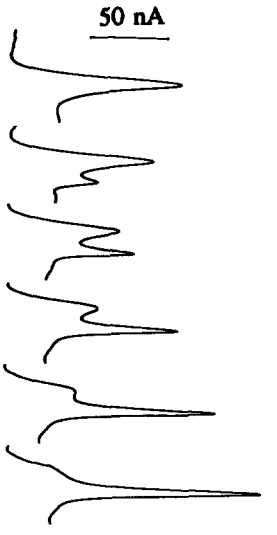

Fig 1 Voltammograms of 0 2μM PCV containing 0, 20, 40, 60, 80, and 100n*M* V, 20m*M* acetate buffer, preconcentration for 60 sec, scan rate of 0 05 V/sec

A very significant enhancement of the voltammetric response was achieved after adsorption of electroactive species onto a HMDE. The AdSV behavior of V–PCV is shown in Fig. 1. The adsorbed free PCV and V–PCV gave well-resolved peaks at the same potentials as in direct voltammetry. Addition of V to the PCV solution resulted in a decrease in the AdSV peak for PCV and an increase in the V–PCV peak. The reaction between the PCV and V was rapid. The V–PCV peak reached a maximum value when equimolar concentrations of the metal and

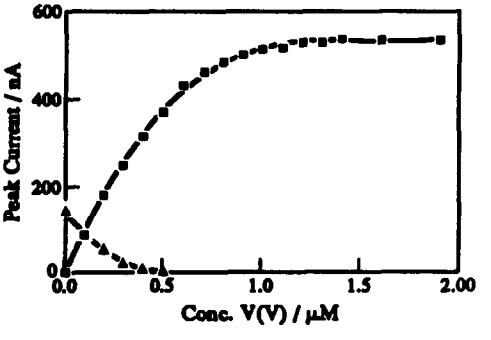

Fig. 2. Peak currents obtained on addition of V to 1μM PCV in 20m*M* acetate buffer, after preconcentration for 30 sec and scan at 0.05 V/sec. ■ V–PCV, ▲ uncomplexed PCV

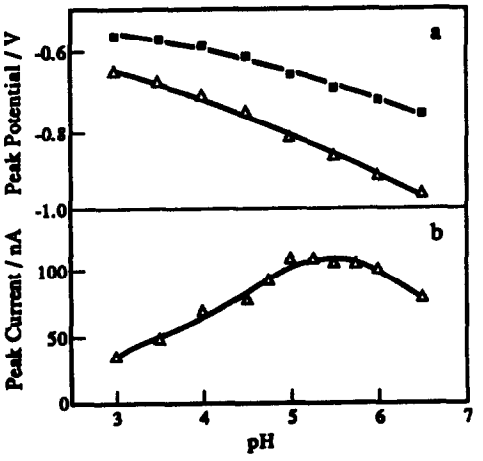

Fig 3. The effect of pH on PCV and V–PCV peak potentials (a) and on V–PCV peak current (b), 25mM acetate buffer, 1μM PCV; 0.1μM V, preconcentration for 60 sec at −0 300 V, scan rate of 0.05 V/sec. ■ PCV, △ V–PCV

ligand were present (Fig. 2) again consistent with a 1:1 complex.

While there have been no previous electrochemical studies of V–PCV complexes, quite extensive spectrophotometric studies have been done. Since almost all published papers deal with ternary complexes (V–PCV–X), there is very little information concerning stoichiometry of binary V–PCV complex in aqueous solutions. In recent work Shijo *et al.*[41] reported that by using acetate buffer at pH 5, the mole ratio of the V:PCV in the binary complex is 1:1. The results we have obtained using conditions specified here are in agreement with this stoichiometry.

The peak current for reduction of an adsorbed species is expected to be dependent upon the scan rate in the voltammetric measurement step. Changing the scan rate from 10 to 200 mV/sec, after deposition for 60 sec in the solution of 0.6μM PCV, 40nM V(V) and 10mM acetate buffer, resulted in a linear increase of the V–PCV reduction current. Since both Faradaic and capacitance charging currents depend linearly on the potential scan rate, one would not expect to influence the ratio of Faradaic-to-charging currents by changing the scan rate.

Triangular wave voltammetry, with and without preconcentration, gave no evidence of any anodic process corresponding to oxidation of the products of reduction.

The peak potential for reduction of the adsorbed complex shifted to more negative values with increasing pH as shown in Fig. 3(a). At the same time, measurement of the peak potentials for PCV and V–PCV showed separation to be maximal at pH 6.5. The V–PCV peak current was a maximum at pH 5.0 as shown in Fig. 3(b).

The V–PCV peak height decreased by about 40% in near linear fashion with increasing acetate concentration from 10 to 100mM. This is probably due to competitive complexation of V by acetate.[42] The recommended buffer concentration of 20mM represents a compromise between a need for sufficient buffer capacity and good sensitivity.

The choice of adsorption time is also a compromise between surface coverage, sensitivity, the time required for an analysis, and the effect of competitive adsorption. The longer the adsorption time, the greater the amount of adsorbed species at a given solution concentration and the greater sensitivity of the measurement. However, if the electrode surface should approach saturation with adsorbed species, the rate of adsorption of the species from solution would be expected to decrease and interaction between the adsorbed species could interfere in the reduction This would reduce sensitivity and produce non-linear calibration curves over a range of V concentration. While a low fractional coverage of the electrode surface with adsorbed species is desirable, the relative error in measurement of adsorption time increases with decreasing time and adsorption times should not be too short. A further complication is evident from the data presented in Fig. 4, which shows how the AdSV peaks for PCV and V–PCV depended on the adsorption time. With a fixed PCV concentration, the V–PCV peak grew with time to a limiting value depending upon the V concentration, suggesting an equilibrium between dissolved and adsorbed com-

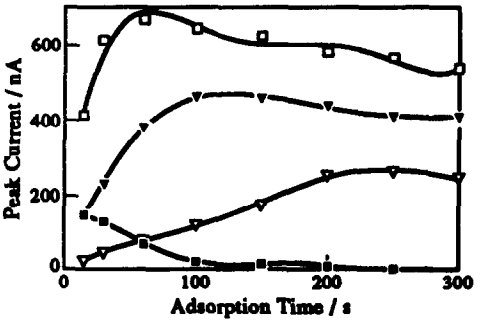

Fig 4 The effect of adsorption time on the voltammetric response for systems containing excess of PCV (3μM PCV in 25mM acetate buffer) and 0.1 (▽), 0.4 (▼), and 1.0 (□) μM V The reduction response of PCV after addition of 0 1μM V is shown as (■) Preconcentration was at −0.300 V and scan rate was 0 05 V/sec

plex. The uncomplexed PCV peak decreased in size over that part of the adsorption time scale where the complex peak was growing. This may indicate that there is competition between free and bound PCV for sites on the Hg drop. However, it is emphasized that all analyses were carried out under conditions of low fractional coverage of the surface. In order to maximize the size of the V–PCV peak with respect to that of free ligand, an adsorption time of 50–100 sec is usually optimum but longer times may be required for very dilute solutions.

The AdSV peak corresponding to surface saturation with V–PCV was a function of the electrolyte composition. In the case of 3.0μM PCV containing 1.0μM V solution, the peak for the V–PCV reduction limited at 665 nA (peak area = 0.71 μC) with a scan rate of 0.05 V sec, using a deposition time of greater than 60 sec. Assuming a two electron reduction, this gives 2.19×10^{12} molecules of V–PCV on the 0.018 cm^2 Hg drop electrode (0.82 nm per V–PCV). The area is near that calculated for surface saturation with other metal complexes in AdSV.[30]

Interferences

Twenty seven different metal ions were tested for interference by adding them individually to a 1.0mM PCV electrolyte containing 0.1μM added V. Of the species tested 1mM Mg(II); 0.5mM Ca(II), Fe(III), Co(II), 0.1mM Tl(I); 20μM Zn(II), Mn(II); and 10μM Sn(II), Cd(II), Hg(II), Pd(II) and Ag(I) did not interfere. Calibration was also carried out in buffered seawater (1.7 dilution) in comparison to similar measurement in distilled water. The linear slope in the former medium was found to be 88% of the latter. This slight suppression of sensitivity would in no way obviate analysis using standard additions calibration. The addition of Th(VI) and U(VI) gave peaks overlapping those for PCV and V–PCV but sensitivity was low and interference was significant only when their concentrations were greater than 0.5μM representing unusually high levels for these elements in aqueous environmental samples. The addition of Cr(VI) produced an interfering peak at −0.90 V, but Cr(III) did not interfere at concentrations up to 20μM. Reduction of the Cr(VI) by the addition of $NH_2OH \cdot HCl$ (0.5mM) removed the interference. Aluminium (III) was found to give a well-defined peak with PCV at the same peak potential as that for reduction of adsorbed V–PCV. However, with 0.3μM citrate there was no peak for Al–PCV and it appeared that citrate complexation of the Al(III) prevented the formation of the PCV complex. The AdSV peak for V–PCV was very little affected by the citrate and it was possible to determine V in the sample which contains Al in 1000-fold excess (see below).

Table 1 AdSV peak potentials and sensitivities for metal–PCV complexes

Metal ion	Reduction potential (V)	Sensitivity ($nA/\mu M$)
Cu(II)	−0 20	400
Pt(IV)	−0 25	95
Rh(III)	−0 25	130
Ir(IV)	−0 30	150
Os(IV)	−0 30	700
Pb(II)	−0 55	320
Ce(IV)	−0 58	35
Mo(VI)	−0 68	60
Ti(IV)	−1 06	310
Ni(II)	−1 18	10

Added Cu(II), Pb(II), Ir(IV), Rh(III), Os(IV), Ce(IV) and Pt(IV) were found to form metal complexes that could be adsorbed and reduced. Those complexes were more readily reduced than PCV itself indicating reduction of the metal centre of the adsorbed complex, the peaks did not overlap with that due to V–PCV. Pyrocatechol violet complexes of Ti(IV), and Ni(II) were reduced at more negative potential than those for PCV and V–PCV, again without overlapping the peak of interest. The Mo(VI)–PCV complex was reduced at a potential between that of PCV and V–PCV and did not interfere with V analysis.

Those metal ions which form complexes with PCV and which can be adsorbed and reduced at potentials different than that for reduction of V–PCV are listed in Table 1 along with their reduction potentials and sensitivities.

The method was also tested for interference from various anionic species. The testing was performed using a 1.0mM PCV solution with 0.2μM added V, and the anions were added as solutions of their Na-salts. The addition of 1mM Cl^-, 3mM SO_4^{2-}, 0.1mM PO_4^{3-} and 0.2mM tartrate did not alter the response with respect to V. The addition of 0.2mM oxalate, 20mM F^-, and 70μM citrate decreased the sensitivity without shifting the potential of the PCV and V–PCV reduction peaks. Addition of V in the presence of each of these species gave linear calibration curves indicating analysis can be done by the method of standard addition.

Surface-active materials present in the elec-

trolyte are also a potential interference. Linear calibration was obtained for V in the presence of surface active material but sensitivity was reduced. On a weight scale the suppressive effect of Triton X-100, a nonionic alkylphenyl–ethoxylate surfactant, was greater than that of a natural humic material. Analysis by standard addition calibration would appear to be valid in the presence of the 1.5 μg/ml of Triton X-100, but it is associated with sensitivity decrease of 35%

Vanadium analysis

The AdSV should be carried out as described in the Experimental section with the V–PCV peak measured from an estimated baseline Calibration of the method should be by standard additions of V(V). Three standard additions with two AdSV measurements after each addition are recommended. The total concentration of V after the addition should not exceed 1μM. For analysis of aqueous samples in the range 10–600nM V, a pH 4.7 electrolyte, 0.02M acetate buffer with 1.0mM added PCV is recommended. Samples with high V concentrations should be diluted to bring them within the recommended concentration range, or alternatively, shorter deposition time may be used Where Al is present in the sample, addition of 10μM citrate to the solution is required.

The 60 sec adsorption gives a low fractional surface coverage of the electrode with adsorbed species. The recommended pH gives a good separation of the peaks for PCV and V–PCV Using standards prepared from the standard V solution, the method gave a linear calibration curve over the range 10–600nM V. The slope of the calibration line (sensitivity) was 1 10 nA/nM/60 sec. The detection limit (DL) was estimated by analysis of a 2nM V standard after deposition of 3 min at the HMDE with area of 2.6 mm^2 and 100 mV/sec scan rate The standard deviation of the signal for eight replicate analyses was $\pm$0.43 nA, giving a detection limit of 0 1nM based on a protection factor of 3 [43]

Analytical results

Using the standard procedure, a number of samples were analyzed for V. The results of analysis of three samples are tabulated in Table 2. The asphalt sample of Venezuelan origin was dry ashed at 550°C for 10 hr, dissolved in 2M HNO_3 and diluted 10-fold prior to the analysis. Comparative Neutron Activation Analysis results obtained on the asphalt samples were generally in good agreement with the AdSV.

One sample was a Sandy Cove sea-water which has been used for the analysis of several other metals although there are no comparative values for V It has been reported that the concentration of dissolved V in uncontaminated sea-water lies in the range 20–60nM,[1] and the results on this sample are within that range. No pretreatment or dilution of the sample was required prior to analysis.

The plant tissue reference material were dry-ashed at 500°C for 8 hr, dissolved in 2M HNO_3 and by a factor of 300 diluted with distilled water before analysis. Even though Al, the most serious interfering element, was in 1000-fold excess the results are in reasonable agreement with the certified value. Because of the large concentration of Al in this material, a concentration of 50μM citrate was added to the analytical solution.

In each case the analyses were carried out at pH 4 7 with measurements on the sample and on the sample after each of three or four standard additions Each measurement was repeated three or four times (9–16 data points per analysis) The confidence intervals reported represent the uncertainty in results derived from extrapolation at the calibration data.

As a comparison, analysis of the sea-water (diluted 1 10 with appropriate buffer) and the plant tissue was attempted using three of the previously-published AdSV methods. With catechol as the complexing agent, no V peak was observed on the sea-water sample This may be due to presence of organic matter as the sample was not UV-irradiated before analysis. For the plant tissue, a concentration of 300 ng/g was determined with standard addition sensitivity of 0.20 nA/nM. Analysis using 5-Br–PADAP in an acetate medium gave no peak for either sample,

Table 2 Analysis of a variety of samples for V content

Source	Measured concentration	Note
Asphalt	624 $\pm$ 53 $\mu g/g$	556 $\pm$ 17 $\mu g/g$*
	725 $\pm$ 34 $\mu g/g$	527 $\pm$ 16 $\mu g/g$*
	655 $\pm$ 44 $\mu g/g$	
Sandy Cove	25 0 $\pm$ 4 4nM	
Sea-water	26 9 $\pm$ 4 3nM	
Plant tissue	435 $\pm$ 40 ng/g	370 $\pm$ 30 ng/g†
	423 $\pm$ 32 ng/g	
	440 $\pm$ 32 ng/g	

*Comparative value by NAA (Slowpoke II)
†Certified value for Plant Tissue Standard Reference Material (Peach leaves SRM 1547)

but the calibration sensitivity was approximately 1.3 nA/nM. When cupferron and BrO_3^- were used, the very high sensitivity of the method was confirmed (sensitivity = 10.2 nA/nM) but again no V peak was observed on either of the samples.

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