

Study on Colour Reaction of Vanadium(V) with 2-(2-Quinolylazo)-5-Diethylaminophenol and Its Application

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ABSTRACT

A sensitive, selective and rapid method has been developed for the determination of vanadium based on the rapid reaction of vanadium(V) with 2-(2-quinolylazo)-5-diethylaminophenol (QADEAP). The QADEAP reacts with V(V) in the presence of citric acid–sodium hydroxide buffer solution (pH = 3.5) and cetyl trimethylammonium bromide (CTMAB) medium to form a violet chelate of a molar ratio 1:2 (V(V) to QADEAP). The molar absorptivity of the chelate is $1.23 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 590 nm in the measured solution. Beer's law is obeyed in the range of 0.01–0.6 $\mu\text{g mL}^{-1}$. This method was applied to the determination of vanadium(v) with good results.

KEYWORDS

2-(2-quinolylazo)-5-diethylaminophenol, vanadium, spectrophotometry.

1. Introduction

Vanadium is an important element, not only for industry, but for biological systems as well.^{1,2} Therefore, a wide variety of spectrophotometric methods for the determination of vanadium have been reported.^{3–10} Each chromogenic system has its advantages and disadvantages with respect to sensitivity, selectivity and rapidity. In previous work, some 2-quinolylazo reagents were reported for the determination of metal ions.^{11–17} This type of reagent has higher sensitivity than pyridylazo reagents because of its larger conjugated system. However, the utilization of 2-quinolylazo reagents for the determination of vanadium has not been reported yet. In this paper, we firstly studied the colour reaction of 2-(2-quinolylazo)-5-diethylaminophenol (QADEAP) with vanadium(V). Based on this, a highly sensitive, selective and rapid method for the determination of vanadium in alloy, water and biological samples was developed.

2. Experimental

2.1. Experimental Apparatus

A UV-160A spectrophotometer (Shimadzu, Japan) equipped with 1 cm microcells (0.5 mL) was used for all absorbance measurements. The pH values were determined with a Beckman Φ -200 pH meter.

2.2. Reagents

All of the solutions were prepared with ultra-pure water obtained by a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA).

QADEAP was synthesized by our laboratory according to the following procedure: 2-aminoquinoline (6.9 g; 0.048 mol) was dissolved in 500 mL anhydrous ethanol. To this solution, sodamide (2.0 g; 0.051 mol) was added and the mixture was refluxed in boiling water bath for 5 h, followed by the addition of isoamyl nitrite (7.4 mL). The solution was refluxed for 30 min on

a boiling water bath, then the solution was cooled and placed over night under 0°C. The diazo salt was obtained by filtering this solution with an isolation yield of 92%. The diazo salt was dissolved in 200 mL anhydrous ethanol, followed by the addition of *m*-diethylaminophenol (6.6 g; 0.042 mol). The carbon dioxide was sparged into the solution with stirring until the pH reaches to about 8.0. The solution stood for two days, before it was diluted with 400 mL of water and extracted with chloroform. The chloroform was evaporated and the residue was re-crystallized with 30% ethanol. The QADEAP was obtained with a yield of 28%. The structure of QADEAP was verified by elemental analysis, IR, ¹HNMR and MS. Elemental analysis: C₁₉H₂₀N₄O found (calculated) C 71.06 (71.23), N 17.13 (17.49), H 6.47 (6.29). IR (KBr) (cm⁻¹): 3610 (ν_{O-H}); 1050 (ν_{C-O}); 1615, 1570, 1510, 1420 (ν_{C=C}); 1375, 1326 (ν_{C-N}); 2920, 2873 (ν_{C-H}); 1465, 1380 (δ_{C-H}); 3070, 3016 (σ_{Ar-H}); 1175, 1120, 865, 775, 730 (δ_{Ar-H}). ¹HNMR (solvent: d₆-acetone) (δ ppm): 1.25 (t 6H, C-CH₃); 2.75 (q 4H, N-CH₂), 2.25 (s 1H, -OH); 6.86–7.85 (m 9H, Ar-H). MS: 320 (M⁺).

A $1.0 \times 10^{-4} \text{ mol L}^{-1}$ of QADEAP solution was prepared by dissolving QADEAP with 95% ethanol. A stock standard solution of vanadium (1.0 mg mL^{-1}) was obtained from Chinese Standard Center, and a work solution of $2.0 \mu\text{g mL}^{-1}$ was prepared by diluting this solution. Citric acid–sodium hydroxide buffer solution (0.5 mol L^{-1} , pH = 3.5 — containing 0.1 mol L^{-1} Na₂EDTA and 0.5 mol L^{-1} NH₄F) was prepared by dissolving 86 g of citric acid (C₆H₈O₇), 32.7 g of ethylenediamine tetraacetic acid disodium salt (C₁₀H₁₄N₂Na₂O₈·2H₂O) and 20.5 g NH₄F in 600 mL of water, then the solution was neutralized to pH 3.5 with 20% sodium hydroxide, and diluted to the volume of 1000 mL. Cetyl trimethylammonium bromide (CTMAB) solution (1.0% (w/v)) was prepared by dissolving CTMAB with 20% ethanol. All chemicals used were of analytical grade unless otherwise stated.

2.3. General Procedure

To a standard or sample solution containing no more than 15 μg of V(V) in a 25 mL calibrated flask, 4 mL of citric acid–

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Table 1 The effect of surfactants on V(V)-QADEAP chromogenic system.

Surfactant	Absence	CTMAB	CPB	TritonX-100	Emulsifier-OP	Tween-80	Tween-20
λ_{\max} (nm)	584	590	590	586	586	586	586
ϵ ($\times 10^4$) L mol ⁻¹ cm ⁻¹	8.76	12.3	10.7	9.02	8.75	9.08	8.68

sodium hydroxide buffer solution (containing 0.1 mol L⁻¹ Na₂EDTA and 0.5 mol L⁻¹ NH₄F), 3.0 mL of 1.0×10^{-4} mol L⁻¹ QADEAP solution and 1.0 mL of 1.0% CTMAB solution were added. The mixture was diluted to a volume of 25 mL and mixed well. After 10 min, the absorbance of this solution was measured at 590 nm in a 1 cm cell against a reagent blank prepared in a similar way without vanadium.

3. Results and Discussion

3.1. Absorption Spectra

The absorption spectra of QADEAP and its V(V) complex under the optimum conditions are shown in Fig. 1. The absorption peaks of QADEAP and its complex at pH 3.5 are located at 468 nm and 590 nm, respectively.

3.2. Effect of Acidity

Results showed that the optimal pH for the reaction of V(V) with QADEAP is 2.2–5.5. A citric acid–sodium hydroxide buffer solution of pH 3.5 was recommended to control pH. As the use of 3.5–6.0 mL of the buffer solution (pH 3.5) per 25 mL of final solution was found to give a maximum and constant absorbance. The use of 4.0 mL buffer solution was recommended. The buffer solution containing 0.08–0.15 mol L⁻¹ of Na₂EDTA and 0.4–0.6 mol L⁻¹ of NH₄F could markedly increase the selectivity of this system. (Without Na₂EDTA and NH₄F in the buffer solution, the tolerance limits of foreign ions were 0.01 mg for Cu(II), Fe(III), Zn(II); 0.005 mg for Sn(IV), Pd(II), Co(II), Ni(II). However, the tolerance limits of foreign ions reached 10 mg for Fe(III); 0.5 mg for Cu(II), Zn(II); 0.2 mg for Co(II), Ni(II), Sn(IV); 0.1 mg for Pd(II) when Na₂EDTA and NH₄F were present in the buffer solution). Therefore, 0.1 mol L⁻¹ of Na₂EDTA and 0.5 mol L⁻¹ of NH₄F in the buffer were recommended.

3.3. Effect of Surfactants

The V(V)-QADEAP complex has a poor solubility in water solution. One needs to add a suitable amount of surfactants to enhance the solubility of the complex. Experiments showed that all the anionic surfactants, nonionic surfactants and cationic surfactants enhanced the solubility. In addition to enhancing the solubility, in the nonionic surfactants and cationic surfactants medium, the sensitivity of the V(V)-QADEAP chelates was increased markedly too. The effect of the nonionic surfactants and cationic surfactants improving the sensitivity is shown in Table 1. The results show that CTMAB was the best additive and the use of 0.6–3.0 mL of CTMAB gives a constant and maximum sensitivity. Accordingly, 1.0 mL CTMAB solution was recommended.

3.4. Effect of QADEAP Concentration

For up to 15 μ g of V(V), the use of about 3 mL of 1.0×10^{-4} mol L⁻¹ of QADEAP solution has been found to be sufficient for a complete reaction.

Accordingly, 3.0 mL of QADEAP solution was added in all further measurements.

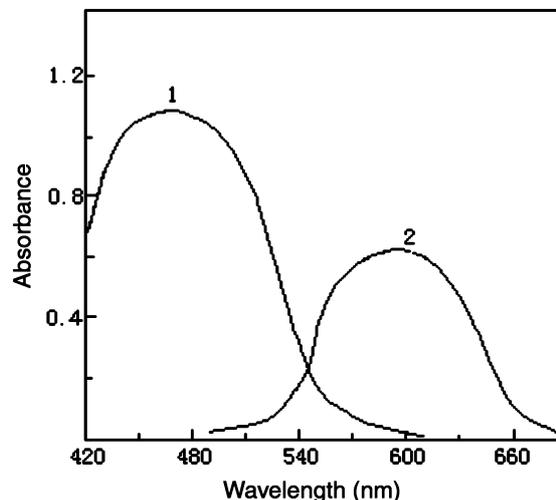


Figure 1 Absorption spectra of QADEAP and its V(V) complex: 1, QADEAP-CTMAB blank against water; 2, QADEAP-V(V)-CTMAB complex against reagent blank.

3.5. Stability of the Chromogenic System

After mixing the components, the absorbance reaches its maximum within 10 min at room temperature and remains stable for at least 16 h.

3.6. Calibration Curve and Sensitivity

The calibration curve (Fig. 2) shown that Beer's law is obeyed in the concentration range of 0.01–0.6 μ g V(V) per mL in the measured solution. The linear regression equation obtained was: $A = 2.426 C$ (μ g mL⁻¹) + 0.0206, ($r = 0.9994$). The molar absorptivity was calculated to be 1.23×10^5 L mol⁻¹ cm⁻¹ at 590 nm.

3.7. Composition of the Complex

The composition of the complex was determined by the continuous variation and molar ratio method. Both showed that the molar ratio of V(V) to QADEAP is 1:2.

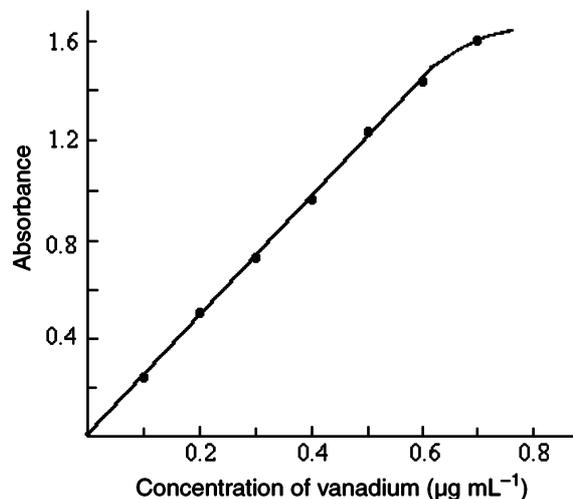


Figure 2 The calibration curve.

Table 2 Tolerance limits for the determination of 5 µg of V(V) with QADEAP (relative error ±5%).

Ion added	Limit amount (mg)
NO ₃ ⁻ , K ⁺ , borate, tartaric acid	80
Li ⁺ , Al ³⁺ , PO ₄ ³⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ , ClO ₄ ⁻	30
Ca ²⁺ , Mg ²⁺ , BrO ₃ ⁻ , B(III), ClO ₃ ⁻ , Fe ³⁺	10
SO ₃ ²⁻ , Sr ²⁺ , Ba ²⁺ , IO ₃ ⁻ , Cr ³⁺ , Fe ²⁺	5
Mn ²⁺ , Ce(IV), W(VI), Mo(VI)	2
Ti(IV), Bi(III), Cr(VI), Zr(IV), Zn ²⁺ , Cu ²⁺	0.5
Tl(III), Cd ²⁺ , La ³⁺ , Sn(IV), Co ²⁺ , Ni ²⁺ , (Pt(IV) * , Ag ⁺ *)	0.2
Ru(III), Bi(III), Pb ²⁺ , Hg ²⁺ , Sb ³⁺ , Pd ²⁺ , Os(VIII)	0.1
Se(IV), Te(IV), Au ³⁺ , S ₂ O ₃ ²⁻ , Zr(IV), Th(IV)	0.05
Ir(IV), Rh(III), Ru(III), U(IV)	0.01
Pt(IV), Ag ⁺	0.005

* Masking with NH₄SCN.

3.8. Interference

The selectivity of the proposed method was investigated by the determination of 5.0 µg 25 mL⁻¹ of V(V) in the presence of various ions within a relative error of ±5%. The results are given in Table 2. Results show that Ag(I) and Pt(IV) give serious interferences. These interferences can be eliminated by masking with NH₄SCN. This method is high selectivity.

3.9. Application

The proposed method has been successfully applied to the determination of vanadium(V) in alloy, biological and water samples.

For biological samples,^{5,18} an appropriate amount of samples was decomposed in a 50 mL round-bottom flask by heating with 20 mL of concentrated nitric acid and 5 mL of 30% hydrogen

peroxide on a hot plate until almost dry. A dropwise addition of concentrated nitric acid was needed to obtain a colourless or yellow residue. The residue was dissolved with 5 mL of water and transferred into a 25 mL calibrated flask. The vanadium contents were analysed spectrophotometrically. The results are given in Table 3.

For a water sample,^{5,18} 300 mL of water was taken and put into a 500 mL flask, and concentrated to about 10 mL by heating on a hot plate. Ten mL concentrated nitric acid and 2 mL of 30% hydrogen peroxide were added in this solution. The mixture was heated on a hotplate and evaporated until almost dry. The residue was dissolved with 8 mL water and transferred into a 25 mL calibrated flask, and analysed spectrophotometrically. The recovery of vanadium was determined by adding 2.0 µg of vanadium to water samples. A standard method using atomic absorption spectrometry was also used as a reference method. The results are given in Table 4.

For low-alloy steel,^{5,18} 0.1 g of steel was accurately weighed, and dissolved in 5 mL of HCl (1:1) and 5 mL of concentrated HNO₃ with gentle heating; 3 mL of perchloric acid and 2 mL of 30% hydrogen peroxide was added, and the solution was carefully evaporated until a dense white fume evolved. This solution was cooled and the adjusted to about pH 11–12 with 10% sodium hydroxide solution. Then the solution was filtered into a 100 mL standard flask and diluted to the mark with water. The vanadium content was determined spectrophotometrically by taking an appropriate volume of this solution. The results are given in Table 5.

4. Conclusion

In this paper, QADEAP was synthesized and the colour reaction of QADEAP with vanadium was firstly studied. QADEAP is

Table 3 Determination of vanadium in certified standard biological samples.

Sample	Standard value (µg g ⁻¹)	This method (µg g ⁻¹)	RSD (%) (n = 5)
Human hair (GBW07601)	As(0.28), B(1.3), Bi(0.34), Ca(2900), Cd(0.11), Ce(1.2), Co(0.71), Cr(0.37), Cu(10.2), Fe(54), Hg(0.36), Mg(360), Mn(6.3), V(1.73), Ni(0.83), Pb(8.8)	1.81	2.4
Tea leaf (GBW08505)	As(0.191), Ba(15.7), Ca(2840), Cd(0.032), Co(0.2), Cr(0.8), Cu(16.2), Fe(373), Hg(0.004), Mg(2240), Mn(766), Ni(7.61), V(3.12), Pb(1.06), Se(0.041), Zn(38.7)	3.05	2.1

Table 4 Determination of vanadium in water samples.

Samples	Vanadium found (ng mL ⁻¹)		RSD (%) (n = 8)	Recovery (%) (n = 5)
	Proposed method	AAS method		
Panlong River water	32.1	35.4	2.1	97
Diangci Lake water	43.2	44.5	2.3	102
Kunming Tap water	16.5	13.8	2.4	98

Table 5 Determination of vanadium I in a certified standard low-alloy steel.

Sample	Standard value (%)	This method (%)	RSD (%) (n = 5)
Steel (GBW01329)	C(0.188), Si(0.305), Mn(1.44), P(0.013), S(0.046), Cr(0.389), Ni(0.166), Cu(0.277), V(0.158), Ti(0.285), Al(0.112), B(0.023)	0.154	1.7
Steel (GBW08532)	C(0.506), Si(1.96), Mn(0.755), P(0.034), S(0.012), Cr(0.102), Ni(0.314), Cu(0.126), V(0.241), Ti(0.352), Al(0.201), B(0.019)	0.243	1.9

one of the sensitive and selective spectrophotometric reagents for vanadium. The molar absorptivity of the chelate reaches $1.23 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. Most foreign ions do not interfere with the determination when masked with Na_2EDTA and NH_4F . Because the QADEAP can rapidly react with vanadium(V) in aqueous solution at room temperature, this method can determine vanadium spectrophotometrically without heating or extraction. This is convenient and rapid. It is a sensitive, selective and convenience method for vanadium.

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