SENSITIVE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH A
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A sensitive and selective method for the determination of vanadium(V) with 2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)phenol (5-Br-PAPS) is described. Vanadium(V) reacts with 5-Br-PAPS in aqueous solution to form a 1:1 complex, which has an absorption maximum at 589 nm. The optimum pH range for the formation of the complex is from 4 to 5, and the molar absorptivity is $5.47 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The log K value of the complex obtained by the ligand exchange method is 16.68. The interference of foreign ions decreases by the addition of cyclohexanediaminetetraacetic acid (CyDTA).

The most common reagents used for the spectrophotometric determination of vanadium are N-benzoyl-N-phenylhydroxylamine¹⁾ and N-benzoyl-N-(o-tolyl)hydroxylamine²⁾. These reagents are generally characterised by high specificity and low sensitivity. The sensitive reagents for vanadium such as chromazurol S³⁾, stilbazo⁴⁾, and pyrocatechol violet⁵⁾ suffer interference from many metal ions. The 4-(2-pyridylazo)resorcinol (PAR)⁶⁾ and its derivatives⁷⁾ react selectively with vanadium in the presence of 1,2-cyclohexanediaminetetraacetic acid (CyDTA), but the solubilities of the reagents are too small.

In this paper, 2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)phenol (5-Br-PAPS) which is a water soluble pyridylazo dye has been used as a spectrophotometric reagent for the determination of vanadium(V). In the proposed method, a colored chelate is formed in moderately acidic medium in the presence of CyDTA. The spectrophotometric characteristics of 5-Br-PAPS for the determination of vanadium(V) and the ligand exchange equilibria between cyclohexanediaminetetraacetatovanadyl(V) and 5-Br-PAPS are reported.

EXPERIMENTAL

Reagent and apparatus

A $1000 \mu\text{g cm}^{-3}$ vanadium(V) solution was prepared by dissolving a definite amount of ammonium vanadate(V) in 0.25 mol dm^{-3} sulfuric acid. The solution was then diluted as required. A $5 \times 10^{-3} \text{ mol dm}^{-3}$ 5-Br-PAPS solution was prepared by dissolving the Dotite 5-Br-PAPS (Dojindo Co., Japan) in water without further purification. A 2 mol dm^{-3} sodium acetate solution was used as a buffer solution. All the other chemicals used were of a guaranteed reagent quality. A Hitachi 100-10 spectrophotometer, a Hitachi 200-20 UV-vis. recording spectrophotometer, and a Hitachi Horiba F-7 pH meter were employed.

Procedure

A sample solution containing 5 μg of vanadium(V) was taken in a 10 cm^3 volumetric flask. To this solution, 1.1 cm^3 of 0.5 mol dm^{-3} sulfuric acid, 1 cm^3 of 0.4 w/v% potassium periodate solution, 0.4 cm^3 of 0.05 mol dm^{-3} CyDTA solution were added. The pH of the solution was adjusted at 4.5 by the addition of 1 cm^3 of 2 mol dm^{-3} sodium acetate solution. After that 0.4 cm^3 of 5×10^{-3} mol dm^{-3} 5-Br-PAPS was added, then the mixture was diluted to 10 cm^3 with water. The absorbance of the solution was measured at 589 nm against the reagent blank.

RESULTS AND DISCUSSION

Absorption spectra

Figure 1 shows absorption spectra of 5-Br-PAPS and its vanadium(V) complex at pH 4.5. The absorption maximum of the complex is seen to lie at 589 nm, and the absorbance of reagent blank at 589 nm is very low. The absorbance of the complex decrease about 7% by the addition of CyDTA. The decrease of absorbance is due to the ligand exchange between VO_2 -5-Br-PAPS and CyDTA. However, CyDTA is practically able to use for masking of many metal ions.

Fig. 1 Absorption spectra of vanadium(V)-5-Br-PAPS complex

1: Vanadium complex without CyDTA

2: Vanadium complex with CyDTA

3: 5-Br-PAPS without CyDTA

4: 5-Br-PAPS with CyDTA

pH: 4.5, V: 1, 2, 0.5 $\mu\text{g cm}^{-3}$; 3, 4, 0 $\mu\text{g cm}^{-3}$; 5-Br-PAPS: 2×10^{-4} mol dm^{-3} ;

CyDTA: 1, 3, 0 mol dm^{-3} ; 2, 4, 2×10^{-3} mol dm^{-3} ; Potassium periodate: 1, 3, 0 w/v%; 2, 4, 0.04 w/v%;

Cell length: 1, 2, 10 mm, 3, 4, 1 mm

Effect of experimental variables

The effect of the pH on the absorbance of the complex was studied on the solutions with or without CyDTA. The results are shown in Fig. 2. The constant, maximum absorbance are obtained in the pH range of 4 to 5 in either case. The absorbance of the complex is constant for at least 1 h.

The effect of 5-Br-PAPS concentration on the absorbance was examined. The results are shown in Fig. 3. The absorbance of the complex is reached the maximum at 1×10^{-4} mol dm^{-3} without CyDTA and 2×10^{-4} mol dm^{-3} with CyDTA, then gradually decreased above these concentrations.

Fig.2 Effect of pH on absorbance of vanadium(V)-5-Br-PAPS complex

1:Without CyDTA; 2:With CyDTA;
 V: $0.5 \mu\text{g cm}^{-3}$;
 5-Br-PAPS: $2 \times 10^{-4} \text{ mol dm}^{-3}$;
 CyDTA: 1,0; $2,2 \times 10^{-3} \text{ mol dm}^{-3}$;
 Potassium periodate: 1,0 w/v%;
 2,0.04 w/v%.

Fig.3 Effect of 5-Br-PAPS concentration on absorbance of vanadium(V) complex

1:Without CyDTA; 2:With CyDTA;
 pH: 4.5, V: $0.5 \mu\text{g cm}^{-3}$;
 CyDTA: 1,0 mol dm^{-3} ; $2,2 \times 10^{-3}$
 mol dm^{-3} ; potassium periodate: 1,0
 w/v%; 2,0.04 w/v%.

Calibration curve, molar absorptivity and sensitivity

A straight-line calibration curve passing through the origin was obtained for the proposed procedure. Molar absorptivity of the complex without CyDTA is $5.47 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and the sensitivity for 0.001 absorbance being 1.0 ng cm^{-2} with CyDTA.

Interferences from foreign ions

Synthetic solutions containing $5 \mu\text{g}$ of vanadium(V), various amount of each of foreign ions to be tested, potassium periodate, and CyDTA were prepared. The vanadium(V) was then determined by the proposed procedure. Among the metals tested, the considerable interferences were from $10 \mu\text{g}$ of cobalt(II) and uranium(VI). However, $200 \mu\text{g}$ of cadmium(II), lanthanum(III), molybdenum(VI), nickel(II), scandium(III), thorium(IV), tin(IV), $100 \mu\text{g}$ of chromium(III), iron(III), lead(II), manganese(II), and zinc(II) were found to be less than 4% of relative error. Interference data are summarized in Table 1.

Table 1 Effect of diverse ions on the determination of vanadium(V)

Ion	Amount	Vanadium(V)	Relative
	added/ μg	found / μg	error, %
		5.0	0
Al^{3+}	200	5.23	+ 4.6
Cd^{2+}	200	4.90	- 2.1
La^{3+}	200	4.80	- 3.9
Mo^{6+}	200	5.18	+ 3.5
Ni^{2+}	200	5.12	+ 2.3
Sc^{3+}	200	5.20	+ 3.9
Sn^{4+}	200	4.98	- 0.5
Th^{4+}	200	4.99	- 0.2
Cr^{3+}	100	5.15	+ 3.0
Fe^{3+}	100	5.15	+ 3.0
In^{3+}	100	5.25	+ 4.9
Mn^{2+}	100	5.15	+ 3.0
Pb^{2+}	100	4.83	- 3.5
Zn^{2+}	100	5.0	0
Cu^{2+}	40	5.22	+ 4.4
Zr^{4+}	40	5.25	+ 4.9
Bi^{3+}	20	5.22	+ 4.3
Co^{2+}	10	5.29	+ 5.8
U^{6+}	10	5.64	+ 12.7

$\text{V(V)} : 5 \mu\text{g}; \text{ pH} : 4.5; 5\text{-Br-PAPS} : 2 \times 10^{-4} \text{ mol dm}^{-3};$

$\text{CyDTA} : 2 \times 10^{-3} \text{ mol dm}^{-3}; \text{ potassium periodate} : 0.04 \text{ w/v}\%.$

Fig.4 Continuous variation method applied to vanadium(V)-5-Br-PAPS complex

$\text{pH} : 4.5;$

$[\text{V}] + [5\text{-Br-PAPS}] : 2 \times 10^{-5} \text{ mol dm}^{-3}$

Composition of the complex

The composition of the complex was estimated by the continuous variation method. Figure 4 shows that the mole ratio of vanadium(V) : 5-Br-PAPS in the complex is found to be 1 : 1.

Ligand exchange equilibria

The following ligand exchange equilibria were studied by photometric means in a similar manner as VO_2PAR ⁸⁾.

Where R denotes 5-Br-PAPS. The conditional ligand exchange constant $K'_{\text{ex}}^{\text{CyDTA}}$ is defined as:

$$K'_{\text{ex}}^{\text{CyDTA}} = \frac{[\text{VO}_2\text{R}][\text{CyDTA}]}{[\text{VO}_2\text{CyDTA}][\text{R}]} \quad (2)$$

The conditional constant $K'_{\text{ex}}^{\text{CyDTA}}$ is correlated to the true ligand exchange constant $K_{\text{ex}}^{\text{CyDTA}}$ of the reaction

$$K_{\text{ex}}^{\text{CyDTA}} = \frac{[\text{VO}_2\text{R}^-][\text{CyDTA}^{4-}]}{[\text{VO}_2\text{CyDTA}^{3-}][\text{R}^{2-}]} = K'_{\text{ex}}^{\text{CyDTA}} \cdot \frac{\alpha_{\text{VO}_2\text{CyDTA}} \cdot \alpha_{\text{R}}}{\alpha_{\text{VO}_2\text{R}^-} \alpha_{\text{CyDTA}}} \quad (4)$$

Where α coefficients are defined as the ratio of the total concentration of the species vs. the concentration of the complete dissociation species, respectively.

Equation (2) can be converted to :

$$\frac{[\text{VO}_2\text{R}^-]}{C_V - [\text{VO}_2\text{R}^-]} = K'_{\text{ex}}^{\text{CyDTA}} \cdot \left\{ \frac{C_R - [\text{VO}_2\text{R}^-]}{C_{\text{CyDTA}} - C_V + [\text{VO}_2\text{R}^-]} \right\} \quad (5)$$

Where C_V , C_R , and C_{CyDTA} denote the total concentration of vanadium, 5-Br-PAPS, and CyDTA species, respectively. Therefore, plots of $\log\{[\text{VO}_2\text{R}^-]/(C_V - [\text{VO}_2\text{R}^-])\}$ vs. $\log\{(C_R - [\text{VO}_2\text{R}^-])/(C_{\text{CyDTA}} - C_V + [\text{VO}_2\text{R}^-])\}$ should be a straight line with a slope of 1. As shown in Fig.5, the value $\log K'_{\text{ex}}^{\text{CyDTA}} = 2.25$ was found at pH 4.6.

Fig.5 Logarithmic plots of eqn. (5)

$C_V : 1.0 \times 10^{-5} \text{ mol dm}^{-3}$;

$C_R : 2.0 \times 10^{-5} \text{ mol dm}^{-3}$;

C_{CyDTA} : variable

The ligand exchange constant K_{ex}^{CyDTA} can be obtained by using the K_{ex}^{CyDTA} value and α coefficients evaluated from the acid dissociation constants of CyDTA³⁾, 5-Br-PAPS ($pK_1 < 1$, $pK_2 = 2.90$, $pK_3 = 11.0$)⁹⁾, $VO_2HCyDTA^{2-}$ ⁸⁾. The value was found to be $K_{ex}^{CyDTA} = 1.23$.

The stability constant of VO_2R was obtained from the constants K_{ex}^{CyDTA} and K_{VO_2CyDTA} as follows:

$$K_{VO_2R} = K_{VO_2CyDTA} \cdot K_{ex}^{CyDTA} = 10^{16.59} \times 1.23 = 10^{16.68} \quad (6)$$

Thus the value of $K_{VO_25-Br-PAPS}$ ($10^{16.68}$) is slightly large or small than that of K_{VO_2CyDTA} ($10^{16.59}$)⁸⁾ or K_{VO_2PAR} ($10^{17.16}$)⁸⁾.

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