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Extraction-Spectrophotometric Determination of Vanadium(V) with Pyrocatechol and N^1-Hydroxy-N^1,N^2-diphenylbenzamidine

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Synopsis. A sensitive procedure for spectrophotometric determination of V(V) with pyrocatechol and N^1-hydroxy-N^1,N^2-diphenylbenzamidine (HDPBA) is described. The value of molar extinction coefficient (ε) of the colored complex in chloroform is 5.60×10^5 dm^3 mol^{-1} cm^{-1} at λ_{max} 410 nm. The optimization of analytical variables, effect of diverse ions and application of the method to environmental samples have been investigated.

Vanadium is reported toxic to human being, animal, and plants .[1-3] Therefore, many sensitive spectrophotometric methods (e.g. xanthene derivative,[4,5] 3,5-dinitrocatechol with brilliant green[6] and rhodamine B,[7] phenylethylenediantipyrinylmethane,[8] diphenylcarbazide,[9] N-(o-sulphonic benzoyl)-N-pyridine (N-(2-pyridyl)-2-sulphobenzamide)[10] and hexadecyltrimethyl ammonium[11]) for determination of V(V) in a variety of complex materials are claimed. Most of these methods suffer from interelemental interferences. In the present investigation, another type of new, selective and sensitive method for the spectrophotometric determination of V(V) with pyrocatechol and N^1-hydroxy-N^1,N^2-diphenylbenzamidine is described. The sensitivity of the present method is comparable to other reported methods whereas the selectivity is seen to be superior.

Experimental

Apparatus. A Varian DMS-100 UV-vis spectrophotometer (double beam) matched with 1 cm quartz cells was used for the absorbance measurements. A Systronic pH meter model-335 was employed for measuring the pH values.

Reagents. All chemicals used were of analytical grade. A standard V(V) stock solution (100 µg V/cm^3) was prepared by dissolving the weighed amount of ammonium metavanadate in double distilled water and standardized as in literature.[12] N^1-hydroxyamidine were prepared as described in literature.[12] A pH 6.0 buffer was prepared by dissolving the appropriate amount of sodium hydroxide–potassium hydrogen phosfate.[13] A 0.4% w/v (0.036 mol dm^{-3}) pyrocatechol in water and 0.4% w/v (0.0138 mol dm^{-3}) N^1-hydrory-N^1,N^2-diphenylbenzamidine solution in ethanol was employed.

Procedure. An aliquot of the solution containing upto 1.0 µg V(V) is taken in a 50 cm^3 beaker and heated with 2.0 cm^3 pyrocatechol and 5.0 cm^3 ethanolic solution of N^1-hydroxyamidine. The pH of the solution is adjusted to 6.0 with sodium hydroxide–potassium hydrogen phosfate buffer (1.0 cm^3) in the 10 cm^3 total solution. The solution is heated over boiling water bath till volume of the solution is reduced to nearly half. Then the cold solution is transferred to a 100 cm^3 separatory funnel by maintaining total aqueous volume to 8.0±2.0 cm^3 with distilled water. The aqueous solution is shaken with 8.0 cm^3 chloroform and the organic phase is separated. The aqueous phase is further washed with 1×2 cm^3 fresh chloroform. All the extract is dried over anhydrous sodium sulfate (2 g) in a 25 cm^3 beaker. All the extract after drying is transferred to 10 cm^3 volumetric flask and filled upto the mark with chloroform. The spectra of the complex formed is scanned against the reagent blank.

Table 1. Spectral Characteristics of Different Species Formed with V(V)+Pyrocatechol or V(V)+Pyrocatechol+HDPBA

Analytical characteristics	Solvent	λ_{max} / nm	ε / dm^3 mol^{-1} cm^{-1}
V(V)+Pyrocatechol (9.0×10^{-3} mol dm^{-3})	Water	420	4650
V(V)+Pyrocatechol (1.6×10^{-1} mol dm^{-3})	Water	590	7600
V(V)+Pyrocatechol (9.0×10^{-3} mol dm^{-3}) (upon heating)+ HDPBA in Chloroform	Chloroform	410	15000
V(V)+Pyrocatechol+ 1 ml ethanol (upon heating) +HDPBA in Chloroform	Chloroform	410	18000
V(V)+Pyrocatechol+ HDPBA in ethanol (at room temperature)	Water–ethanol	410	17500
V(V)+Pyrocatechol+ HDPBA in ethanol (upon heating)	Water–ethanol	390	1.37×10^5
V(V)+Pyrocatechol+ HDPBA in ethanol (upon heating)	Chloroform	410	5.6×10^5

Results and Discussion

Spectral characteristics of the colored complexes formed with V(V)+pyrocatechol, V(V)+N^1-hydroxyamidine, and V(V)+pyrocatechol+N^1-hydroxyamidine at different analytical conditions are summarized in Table 1.

Absorption Spectra. The absorption spectra of the colored complex formed among V(V)+pyrocatechol +HDPBA against the reagent blank in chloroform and that of the reagent blank against chloroform are shown in Fig. 1. The absorption maximum of the colored complex formed, lie at 410 nm. At this region, the reagent blank shows some absorption, hence all the measurements were made against the reagent blank.

Effect of Variables on Formation of the Colored Complex: The effect of pH of the aqueous solution before heating is studied. The optimum pH range is found to be 5.5—6.5. A 40—70% (v/v) ethanol concentration is adequate for maximum color development. Removal of excess of ethanol is necessary in order to prevent miscibility of the aqueous and organic phase. At least 0.005 and 0.007 mol dm^{-3} of pyrocatechol and HDPBA is needed for maximum and constant color development and addition of more pyrocatechol and HDPBA upto 0.01 and 0.017 mol dm^{-3}, respectively cause no adverse effect on the color development of the complex. A heating time of at least 8 min (over boiling water bath) is required for the maximum color development of complex formed in aqueous ethanol solution and prolonged heating upto 15 min cause no adverse effect.

Effect of Variables on the Extraction of the Colored Complex: The colored complex formed among V(V)+pyrocatechol+N^1-hydroxyamidine is quantitatively extractable into chloroform, carbon tetrachloride, benzene, and toluene. Of these, toluene gives the most sensitive color reaction ($\varepsilon=11.0\times10^5$ dm^3 mol^{-1} cm^{-1}, λ_{max} 420 nm) but after 5 min the organic phase becomes hazy probably due to low solubility of N^1-hydroxyamidine. Hence, chloroform (5.60×10^5 dm^3 mol^{-1} cm^{-1}, λ_{max} 410 nm) has been chosen for the extraction of the complex in the present investigation.

The variation of the temperature of the aqueous phase from 15—40 °C cause no change in the absorbance of the extract. The color of the extract is stable for at least 1 h at room temperature (22±2 °C). The volume ratio of the organic to the aqueous phase from 5 : 2 to 1 : 2 do not affect the color intensity of the extract. A shaking time of 2 min is sufficient for maximum extraction.

The optimum concentration range on the basis of Beer's law is found to be 0—1.0 μg V(V)/10 cm^3 in chloroform with a correlation coefficient of 0.98. The molar absorptivity of the colored complex and the limit for detection of the metal are 5.60×10^5 dm^3 mol^{-1} cm^{-1} and 0.1 μg dm^{-3} (more than the absorbance value of the blank and twice of standard deviation of the blank for 10 replicate measurements) at λ_{max} 410 nm, respectively. The relative standard deviation of 10 replicate measurements at level of 0.4 μg V/10 cm^3 in chloroform is found to be ±2% and the confidence limit at 95% probability is $(5.60\pm0.05)\times10^5$ dm^3 mol^{-1} cm^{-1}.

Percentage Extraction. A 10 and 20 μg standard solution of V(V) is taken and color is developed as in the

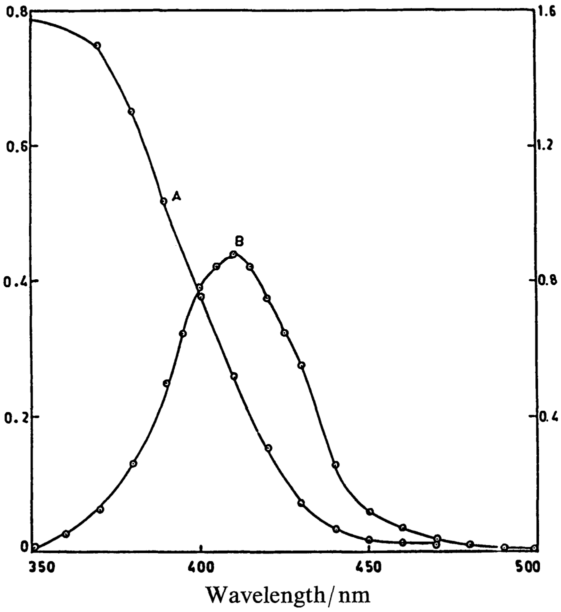

Fig. 1. Absorption spectra of the solvated complex formed by heating V(V) with HDPBA and pyrocatechol as in the procedure.
$C_{pyrocatechol}=9.0\times10^{-3}$ mol dm^{-3},
$C_{HDPBA}=1.4\times10^{-2}$ mol dm^{-3},
pH=6.0±0.2,
(A) Reagent blank.
(B) Vanadium(V) colored complex.
$C_{V(V)}=7.8\times10^{-7}$ mol dm^{-3}.

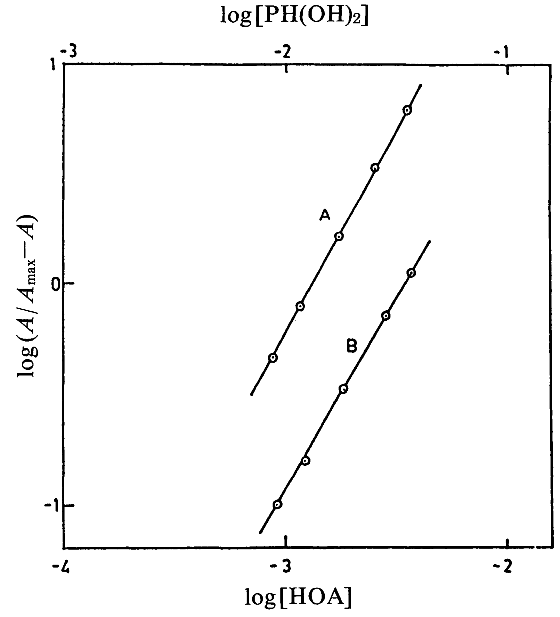

Fig. 2. Determination of ratio of the metal to the reagent in the colored complex.
$C_{V(V)}=9.8\times10^{-7}$ mol dm^{-3}, in the aqueous solution pH=6.0±0.2,
(A) $\log A/(A_{max}-A)$ versus log[pyrocatechol]
$C_{HDPBA}=1.4\times10^{-2}$ mol dm^{-3},
(B) $\log A/(A_{max}-A)$ versus log[HDPBA]
$C_{pyrocatechol}=9.0\times10^{-3}$ mol dm^{-3}.

Table 2. Determination of Vanadium(V) in Environmental Samples

Sample	V(V) found by PAR method[a)]	V(V) found by this method[a)]	Rel. std. dev. of this method
	ppb	ppb	±%
Puri, Orissa, India	26	27	1.8
Jam Nagar, Gujrat, India	9	10	2.2
Adwani Oerlikon, Urla, Raipur	77	79	1.7
Singhania Steel, Urla, Raipur	100	102	1.6
Swastik Wires, Urla, Raipur	68	71	1.8
Allied Steel, Tatibandh, Raipur	34	36	1.9
Super Steel, Sarona, Raipur	49	52	2.0
Blast Furnace, Bhilai (M.P.)	14	16	2.1
Total Waste Water, Bhilai Steel Plant, Bhilai (M.P.)	4	3.5	2.3
Cement dust, CCI, Mandhar (MP)	790	795	1.8
Coal dust, CCI, Mandhar (MP)	1610	1659	1.6

a) Average of five determinations.

procedure. The colored complex is extracted, the extract is evaporated, digested with acids and determined by 4-(2-pyridylazo)resorcinol as in the literature.[15)] The percentage extraction is found to be 98±0.2% in a single extraction.

Stoichiometry of Extraction. The ratio of the metal to pyrocatechol or HDPBA was determined by plotting $\log A/(A_{\max}-A)$ versus log molar concentration of pyrocatechol or HDPBA in the organic solution. The slope for pyrocatechol and HDPBA curves are found to be 1.98 and 1.86, respectively, close to integer 2, suggesting the involvement of vanadium : pyrocatechol : HDPBA in 1 : 2 : 2 ratio in the formation of chloroform extractable colored complex. V(V) is reduced to V(IV),[14)] by means of pyrocatechol to react further with 2 moles each of pyrocatechol and N^1-hydroxyamidine. The probable reaction mechanism can be written as:

$$\mathrm{VO^{2+}+2\,PyO_2^{2-}+2\,HDPBA}+n\,\mathrm{EtOH+2H^+}\rightleftarrows \mathrm{[V(PyO_2)_2]\cdot 2\,HDPBA}\cdot n\,\mathrm{EtOH+2H_2O}$$

The complex so formed is extractable into chloroform

$$\mathrm{[V(PyO_2)_2]\cdot 2\,HDPBA}\cdot n\,\mathrm{EtOH+2H_2O}\rightleftarrows \mathrm{[V(PyO_2)_2]\cdot 2\,HDPBA}\cdot n\,\mathrm{EtOH_o+2H_2O}$$

Where o, $\mathrm{PyO_2^{2-}}$, and HDPBA denote the organic phase, pyrocatechol anion, and N^1-hydroxy-N^1,N^2-diphenylbenzamidine, respectively.

Effect of Diverse Ions: The effect of the diverse ions on the determination of 0.4 μg V(V) was studied as in procedure. No diverse ions were found to interfere in the spectrophotometric determination of the metal. Their tolerance limit are summarized in parenthesis in μgs:
Cu(II) (200), Ag(I) (150), Ba(II) (100), Cd(II) (40), Hg(II) (50), Al(III) (200), La(III) (100), Pb(II) (40), Zr(IV) (200), As(V) (75), Sb(V) (50), Nb(V) (50), Cr(III) (125), W(VI) (50), Fe(III) (50), Co(II) (100), Ni(II) (100), Os(VIII) (25), U(VI) (150), EDTA (400), $\mathrm{F^-}$ (150), $\mathrm{C_2O_4^{2-}}$ (50), $\mathrm{NO_3^-}$ (50), $\mathrm{PO_4^{3-}}$ (400).

Application. The validity of this method is tested to environmental samples e.g. cement dust, coal dust, sea water, and industrial waste water. The solid sample is digested with aqua regia and concentrated hydrochloric acid and the dried residue is dissolved in water. In case of 4-(2-pyridylazo)resorcinol method, the metal is prior separated by extraction with N^1-hydroxy-N^1,N^2-diphenylbenzamidine from 6 mol dm^{-3} $\mathrm{CH_3COOH}$ as described in the literature.[12)] The extract is evaporated, digested by acids treatment, dissolved in water and determined spectrophotometrically by 4-(2-pyridylazo)resorcinol.[15)] The metal content analysed by these two procedures are comparable (Table 2).

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