

Sodium dodecyl sulfate 에서 2-Hydroxybenzaldehyde-5-Nitro-pyridylhydrazone을 이용한 바나듐(IV)의 분광광도법 정량

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(1999. 8. 27 접수)

Spectrophotometric Determination of Vanadium(IV) with 2-Hydroxybenzaldehyde-5-Nitro-pyridylhydrazone in the Presence of Sodium Dodecyl Sulfate

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(Received August 27, 1999)

요 약: 2-Hydroxybenzaldehyde-5-nitro-pyridylhydrazone (2HB-5NPH)를 합성하여 계면활성제 하에서 바나듐 이온(IV)의 분광학적 정량에 응용하였다. pH, 용매효과, 리간드 농도와 계면활성제의 최적조건을 구하였다. 이 과정을 혼합 시료와 실제 시료 중의 바나듐(IV) 정량에 적용하여 만족한 결과를 얻었다(회수율 $\geq 97\%$; $0 \sim 1.5 \mu\text{g/mL}$ 농도 범위에서 상대 표준 편차 $\leq 3.0\%$; 용액중에서 검출 한계 $0.02 \mu\text{g/mL}$).

Abstract: 2-Hydroxybenzaldehyde-5-Nitro-pyridylhydrazone (2HB-5NPH) was synthesized and its application in the spectrophotometric determination of vanadium ion(IV) was studied in the presence of surfactant. The optimum conditions of pH, solvent effect, concentration of ligand and surfactant were evaluated. The procedure was applied to determination of vanadium(IV) in mixture sample and real sample with satisfactory results (recovery $\geq 97\%$; relative standard deviation $\leq 3.0\%$ in the concentration range of $0 \sim 1.5 \mu\text{g/mL}$; detection limit, $0.02 \mu\text{g/mL}$ in solution).

Key word: Vanadium(IV), 2HB-5NPH, SDS, spectrophotometric determination

1. Introduction

Vanadium at ng/mL levels is an essential trace element possessing specific physiological functions, but it can be toxic when present at $\mu\text{g/mL}$ concentrations. In environmental chemistry, vanadium is one of the most important elements acting as a tracer in the evaluation of air pollution caused by fossil fuel combustion.¹

Vanadium in environmental samples has generally been determined by conventional² or catalytic,³ atomic absorption spectrophotometry,^{4,5} x-ray fluorescence spectro-metry,⁶ neutron activation analysis,⁷ reversed-

phase liquid chromatography⁸ and spectrophotometry.⁹⁻¹⁸ These methods have not enough selectivity for the various oxidation states of vanadium.

In the previous work,¹⁹ the author synthesized 2-hydroxybenzaldehyde-5-nitro pyridylhydrazone (2HB-5NPH), and it showed a sensitive spectrophotometric reagent for Co(II). This paper describes the spectrophotometric determination of V(IV) by 2HB-5NPH in methanol medium. Moreover the influence of the anionic surfactant (sodium dodecyl sulfate) on the absorbance of the V(IV)-2HB-5NPH complex has been investigated and a very sensitive spectrophotometric method for the determination of V(IV) is proposed. The application of the method to the analysis of water samples is also demonstrated.

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2. Experimental

2.1. Reagent and Apparatus

Analytical-reagent grade chemicals and, distilled and deionized water were used throughout.

A stock standard solution of vanadium (50 ppm) was prepared from V(IV) AAS standard solution and working standard solutions were prepared by dilution. An acetic acid-sodium acetate buffer solution (pH 6.5) was used. Surfactants were from Sigma Co. and used without further purification. Surfactant solutions ($1.0 \times 10^{-2}M$) were prepared by dissolving suitable amounts of surfactants in water with gentle heating.

2-Hydroxybenzaldehyde-5-Nitro-pyridylhydrazone ($1.0 \times 10^{-3}M$) was prepared by dissolving 0.258 g of the reagent in 1000 mL of absolute methanol. The following buffered solutions were prepared : hydrochloric acid-potassium hydrogen phthalate (pH 1~3); acetic acid-sodium acetate (pH 3~6); potassium dihydrogen phosphate-sodium hydroxide (pH 7).

All absorbance measurements were made with a Perkin-Elmer 552S Spectrophotometer using 1-cm quartz cells. All pH measurements were made with a NOVA-310 pH Meter. A Hitachi IR 435 Infrared Spectrophotometer and Yamato Model MP-1 melting point were used.

2.2. Procedure

The synthesis of 2-Hydroxybenzaldehyde-5-nitro-pyridylhydrazone has been described previously.¹⁹

2.3. Spectrophotometric determination

An appropriate amount of sample solution or standard V(IV) solution transferred to a 50 mL volumetric flask. 5.0 mL of the $1 \times 10^{-3}M$ 2HB-5NPH methanol solution, 5.0 mL of acetic acid-sodium acetate buffer solution (pH 6.5) and 1.0 mL of $5.0 \times 10^{-2}M$ surfactant solution were added, then filled the volume to the mark with methanol. The absorbance of the solution was measured at 300~600 nm against a reagent blank as a reference.

3. Results and Discussion

Vanadium(IV) reacts with 2HB-5NPH giving a pale yellow color in neutral medium which is intensified in weak acidic solution. The spectral characteristics, effect

of variables and diverse ions on V(IV)-2HB-5NPH absorbance and applications of the system are discussed below.

3.1. Absorption spectra

The absorption spectra of 2HB-5NPH and V(IV)-2HB-5NPH complex were recorded as shown in Fig. 1. The absorption maximum of the reagent lies at 388 nm (2HB-5NPH) and that of the complex at 474 nm which was chosen for the measurements, because sensitivity at this wavelength is higher and the absorbance of the reagent itself is very small.

The influence of the pH on the absorbance of the V(IV)-2HB-5NPH complex is shown in Fig. 2, which shows that the maximum absorbance of the V(V)-2HB-

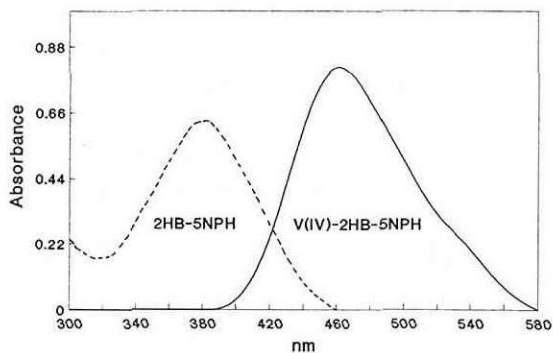


Fig. 1. Absorption spectra of V(IV)-2HB-5NPH solution. V(IV) : 1.0 $\mu g/mL$, 2HB-5NPH: $1.0 \times 10^{-4}M$, pH 6.5.

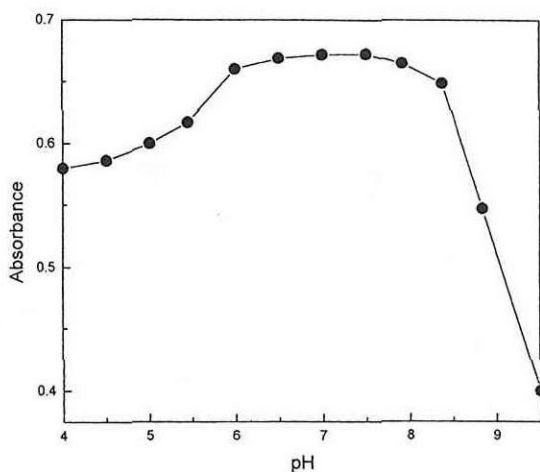


Fig. 2. Effect of pH on V(IV)-2HB-5NPH complex. V(IV) : 1.0 $\mu g/mL$, 2HB-5NPH: $1.0 \times 10^{-4}M$.

5NPH complex appears at pH of the range 6.3~6.8. Excepting these pH range, the absorbance of all decreased. So, pH 6.5 was selected for experiments.

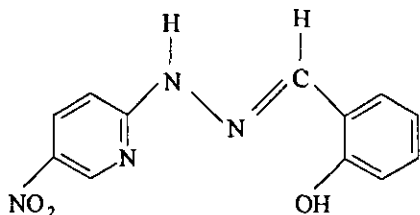
3.2. Effect of solvent and reagent concentration

The effect of various solvents such as *n*-butyl alcohol, isobutyl alcohol, ethanol, acetone and methanol on the absorbance of V(IV)-2HB-5NPH was studied. The solution of 85 ± 2% (v/v) methanol and 15% water was found to be the best solvent for the system.

The influence of the amount of 2HB-5NPH on the absorbance of solution containing 1.0 ppm of V(IV) was studied under the conditions established above. The optimal concentration of 2HB-5NPH was 5 mL (1.0×10^{-4} M). Thus, 1.0×10^{-4} M was selected to ensure a sufficient excess of the reagent throughout the experimental work.

3.3. Effect of surfactant concentration

The effects of various surfactants were studied. The effects of cationic surfactants [cetyltrimethylammonium bromide (CTMAB), dodecyltrimethylammonium bromide (DTMAB)], nonionic surfactants [Brij 35, Brij 58, Triton X-100] and anionic surfactant [sodium dodecyl



Scheme 1.

Table 1. Absorbance characteristics of V(IV)-2HB-5NPH complex in the different surfactants
V(IV): 1.0 ppm, 2HB-5NPH: 1.0×10^{-4} M, pH 6.5

Surfactant	Concentration(M)	max(nm)	Absorbance
None	-	476	0.821
CTMAB	1×10^{-3}	460	0.846
DTMAB	1×10^{-3}	468	0.845
SDS	1×10^{-3}	454	0.953
Triton X-100	1×10^{-3}	462	0.857
Brij 35	1×10^{-3}	464	0.800
Brij 58	1×10^{-3}	464	0.778

sulfate (SDS)] on the V(IV)-2HB-5NPH complexes were studied. As shown in Table 1, the anionic surfactants had a increase of absorbance but in the nonionic and cationic surfactants showed no effect or diminished on the absorbance of the V(IV)-2HB-5NPH complex. As shown in Table 1, the use of the surfactant of sodium dodecyl sulfate (SDS) as anionic surfactant was most effective in improving absorbance, and the color development was stable and reproducible.

The absorbance increased with an increase of SDS concentration until 1.0×10^{-4} M, but the absorbance diminished with further increase of SDS. So, 1.0×10^{-4} M of SDS was selected for further investigations.

3.4. Characteristics of the complex

The V(IV)-2HB-5NPH complex could be formed immediately at 10~30°C. The absorbance of the complex could be stable for at least 2 hr under 25°C.

We measured the mole ratio of V(IV) and 2HB-5NPH in V(V)-2HB-5NPH complex with and without SDS. The mole ratio of V(IV) and 2HB-5NPH in the V(IV)-2HB-5NPH complex was determined by continuous variation method with measurement of the absorbance of each solutions containing different volume fraction of V(IV) and 2HB-5NPH of same concentration. And, the mole ratio of V(IV)-2HB-5NPH complex in the presence of 1.0×10^{-3} M SDS was also determined. The mole ratio of V(IV) and 2HB-5NPH in the V(IV)-2HB-5NPH complex regardless of the existence of SDS is 1:2.

3.5. Calibration graph

The calibration graph obtained by the general procedure gives good linearity over the range 0~1.5 µg mL⁻¹. The molar absorptivity was calculated as a 4.6×10^4 mol⁻¹cm⁻¹L. The detection limit (S/N=3) was 0.02 µg mL⁻¹ and the relative standard deviation at the 0.5 µg mL⁻¹ V(IV) level was 3.0% (n=7). The addition of SDS to the V(IV)-2HB-5NPH system results in 1.5-fold improvement of the detection limit.

3.6. Effect of foreign ions

To assess the usefulness of this method, the effects of foreign ions which often interfere the determination of V(IV) were studied. The tolerance limits given in Table

Table 2. Tolerance limit of various ions on the recovery of 0.5 ppm V(IV)

Tolerance limit (ppm)	Foreign ions
2000	K(I), Na(I), Cl ⁻ , NO ₃ ⁻ , ascorbic acid
150	sodium thiosulfate, citric acid
100	Ca(II), oxalic acid
5.0	Pb(II)
2.5	Zr(IV), Er(III), Sm(III), Eu(III), UO ₂ (II), Pt(III), Sn(II)
1.0	Ti(IV), Sc(III), Mo(IV), Tb(III), Au(III), Cd(II)
0.5	Ni(II), Al(III), Pd(II), Ge(IV), Zn(II)
0.1	Fe(III), Co(II), Cu(II)

Table 3. Recovery assay Vanadium in synthetic samples*

Sample	Composition	Concentration (ppm)	max (nm)	Absorbance
A	V(IV)	1.0	454	0.954
B	V(V)	1.0	455	0.836
C**	V(IV)+V(V)	0.5+0.5	454	0.950

* Measured under the same conditions as used for the calibration.

** V(V) reduced to V(IV) using ethanol such as reductant in the presence of 1.0N H₂SO₄.

2 are the concentrations that cause error of less than $\pm 5.0\%$ in the absorbance of 0.5 ppm V(IV) solution. 2HB-5NPH forms a stable complexes with various metal ions including transition metal ions. Especially with Fe(III), Co(II) and Cu(II) reacted 2HB-5NPH to form complexes with large molar absorptivities.

3.7. Reduction of vanadium(V)

The absorbance of V(V) decreased about 12% for V(IV) on the proposed method. So, for the simultaneous determination of V(IV) and V(V), V(V) reduced to V(IV), using ethanol as a reductant in the presence of 1.0N H₂SO₄.²⁰ The result of reduction was tested with diphenylamine. The results are shown in Table 3.

3.8. Applications

3.8.1. Determination of vanadium in synthetic mixtures by masking agent

Table 4. Determination of V(IV) in some synthetic mixtures

Sample	Composition of mixture (ng/mL)	V(IV) (ng/mL)	
		Found ^a	Recovery \pm SD ^b
A	V(IV)(250)	250	100 \pm 0.0
B*	A+Fe(1000)	248	99 \pm 1.2
C*	A+Fe(1000)+Ni(2000)	255	102 \pm 1.8
D**	A+Cu(2000)	270	108 \pm 3.5
E***	A+Co(1000)	240	96 \pm 2.5

^aAverage of four replicate determinations.

^bThe measure of precision is the SD.

*Masked by potassium cyanide (7.5×10^{-4} M).

**Masked by thiosulphate (7.5×10^{-2} M).

***Masked by oxalic acid(5.0×10^{-2} M).

Several synthetic mixtures of varying compositions containing V(IV) and other ions of known concentrations were determined by the present method using oxalate, thiosulphate and cyanide as masking agent. A 4-fold excess of Co(II) could be tolerated using 5.0×10^{-2} M of oxalate as a masking agent. The interference due to Cu(II) ion up to 8-fold can be eliminated by using 7.5×10^{-2} M of thiosulphate. And, the interference of Fe(III) could be removed by adding 7.5×10^{-4} M of potassium cyanide. The results are shown in Table 4.

3.8.2. Determination of vanadium in water samples

The usefulness of the proposed method was evaluated by the determination of vanadium in tap, river and sea water samples. Tap and river water (in which V(IV) concentration was not detectable with the proposed method) were spiked with V(IV) at different concentration levels and analyzed. 1 L of water sample was taken and 5 mL of concentrated H₂SO₄ was added to it. The solution was heated to almost dryness on the hot plate. The residue was dissolved in 20 mL of 1 M HCl and finally, the solution was made up to 50 mL with distilled water in a calibrated volumetric flask. An aliquot of this sample solution was taken individually and analyzed by the general procedure after Fe(III), Cu(II) and Co(II) were masked with cyanide-oxalate-thiosulphate. The results are shown in Table 5. The recovery of vanadium was 95-105% and the R.S.D. < 3.0%.

4. Conclusion

This method is one of the most sensitive

Table 5. Recovery study of spiked V(IV) in tap, river, sea water

Sample	Contents of other element (ng/mL)	This method ^a			ICP
		V(IV) spiked (ng/mL)	V(IV) recovered (ng/mL)	Recovery (%)	V(IV) found (ng/mL)
Tap water (laboratory)	Co(-), Cd(-)				
	Al(194), Fe(124)	100	105 ± 3	105	99
	Cu(12), Ni(1.7) Pb(17)	250	244 ± 5	97.6	250
River water	Co(-), Cd(0.4)				
	Al(370), Fe(500)	100	95 ± 3	95	100
	Cu(36), Ni(2.7) Pb(35)	250	242 ± 5	97	249
Sea water	Co(4.1), Cd(1.4)				
	Al(112.1), Fe(69.8)	0	6.5 ± 0.2	104.8	6.2
	Cu(15.3), Ni(7.3) Pb(37.2)	100 250	110 ± 3 259 ± 5	103.6 101.2	106 257

^aAverage of three determinations.

determination methods of vanadium and is excellent in terms of simplicity. No extraction step is required and hence the use of organic solvents, which are generally toxic pollutants, is avoided. The proposed methods should be useful for assay of trace amounts of V(IV) ion in various water samples.

Acknowledgment

This work was supported by 1998 Research Foundation of Inha University.

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