

NOTE

Direct Spectrophotometric Determination of Vanadium(V) Using a Recently Synthesized Hydroxytriazene Derivative

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A new hydroxytriazene (3-hydroxy-3-*p*-chlorophenyl-1-*p*-nitrophenyl-triazene) has been prepared. The reagent has been used for spectrophotometric determination of vanadium(V). Vanadium forms a 1 : 1 yellowish green complex with this reagent. The complex shows maximum absorbance at 410 nm (λ_{max}) in the pH range of 7–9. Beer's law for determination of vanadium is obeyed in the concentration range of 0.51–3.06 $\mu\text{g mL}^{-1}$. Molar absorptivity and Sandell's sensitivity were found as 7463 $\text{L mol}^{-1} \text{cm}^{-1}$ and 6.83 ng cm^{-2} , respectively. Standard deviation (σ) using ten determinations was found to be 0.009 $\mu\text{g mL}^{-1}$ for 2.55 $\mu\text{g mL}^{-1}$ of vanadium.

Key Words: Spectrophotometric determination, Vanadium(V), Hydroxytriazene.

Survey of literature reveals that the work done on hydroxytriazene has been reported in the four reviews^{1–4}. The aim of this work was the development of a simple and efficient spectrophotometric determination method for vanadium(V) ion using a recently synthesized hydroxytriazene derivative (3-hydroxy-3-*p*-chlorophenyl-1-*p*-nitrophenyltriazene) as a chromogenic reagent.

The absorbance measurements were carried out with a Shimadzu UV-160 spectrophotometer at 410 nm (λ_{max}) and pH determinations were performed using a Jenway 302P pH meter. Vanadium stock solution ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving an appropriate amount of sodium metavanadate (AR) in double distilled water and standardized with ferrous ammonium sulfate using diphenylamine as indicator⁵. Working solutions were prepared by appropriate dilution. The new reagent was synthesized by coupling diazotized *p*-nitroaniline hydrochloride with *p*-chloronitrobenzene hydroxylamine at 0.0°C. pH was kept around 5.0 by addition of saturated sodium acetate as needed and crude product was 41 g (m.p. = 131°C, yellow colour). Reagent solutions of desired concentrations were prepared by dissolving requisite quantities in ethanol. The pH of the complex was adjusted using 1% (m/v) aqueous solution of acetic acid. The elemental analysis of the compound revealed m.f. ($\text{C}_{12}\text{H}_9\text{N}_4\text{O}_3\text{Cl}$). Anal. (Calcd.) %: C, 49.29 (49.25); H, 3.27 (3.10); N, 18.82 (19.14).

Absorption Spectra

Under optimal experimental condition, six-fold excess of reagent was added to an aliquot containing 0.51–3.06 $\mu\text{g mL}^{-1}$ of V(V) and the solution was diluted to 10

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mL with ethanol. The development of yellowish green colour of complex is instantaneous and remains stable for many hours. The complex shows maximum absorbance at 400 nm and for subsequent measurements the wavelength 410 nm was used where the absorbance of reagent is minimum. Absorbance measurements were made against a reagent blank.

The composition of the complex was determined using Job's method⁶, slope ratio method⁷, Yoe and Jones mole ratio method⁸, as well as Zolotov's mole ratio method⁹. The composition of the complex has been found to be 1 : 1 (V : V) by all the four methods. Beer's law is obeyed in the concentration range of 0.51–3.0 $\mu\text{g mL}^{-1}$ of vanadium. The molar absorptivity and Sandell's sensitivity were found as 7463 $\text{L mol}^{-1} \text{cm}^{-1}$ and 6.83 ng cm^{-2} respectively at 410 nm. The standard deviation (σ) was obtained by measuring the absorbance of ten solutions and was found to be 0.009 $\mu\text{g mL}^{-1}$ for 2.55 $\mu\text{g mL}^{-1}$ of vanadium.

Stability Constant: Harvey and Manning method¹⁰ (using mole ratio curve) has been used to determine the stability constant of the complex. Thus, the values of $\log \beta$ and ΔG were found to be 5.12 and $-7.66 \text{ kcal mol}^{-1}$ respectively.

Effect of Diverse Ions: Interference due to 5.0 $\mu\text{g mL}^{-1}$ of 21 diverse ions was studied in the determination of 2.55 $\mu\text{g mL}^{-1}$ of vanadium. For those ions which did not interfere at 5.0 $\mu\text{g mL}^{-1}$ levels, the interference was further studied at 10.0, 50.0, 75.0 and 100.0 $\mu\text{g mL}^{-1}$ levels. It was found that in the determination of 2.55 $\mu\text{g mL}^{-1}$ of V(V); Na^+ , K^+ , NH_4^+ , Ni^{2+} , Mg^{2+} , Ba^{2+} , Mn^{2+} , Cu^{2+} , F^- , Br^- , I^- , CH_3COO^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, NO_2^- , Cl^- do not interfere when present in 5.0 $\mu\text{g mL}^{-1}$; Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ba^{2+} , F^- , Br^- , I^- , CH_3COO^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, Cl^- and NO_2^- do not interfere when present in 10.0 $\mu\text{g mL}^{-1}$; Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ba^{2+} , F^- , Br^- , I^- , CH_3COO^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, Cl^- do not interfere when present in 50.0 $\mu\text{g mL}^{-1}$ level; Na^+ , K^+ , NH_4^+ , F^- , Br^- , I^- , CH_3COO^- , NO_3^- , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$ and Cl^- do not interfere when present in 75.0 $\mu\text{g mL}^{-1}$ level and Na^+ , K^+ , NH_4^+ , F^- , Br^- , CH_3COO^- , NO_3^- , CO_3^{2-} , and Cl^- do not interfere when present in 100.0 $\mu\text{g mL}^{-1}$ concentration. However Cd^{2+} , Zn^{2+} and Co^{2+} interfere seriously even when present in 5.0 $\mu\text{g mL}^{-1}$ concentrations. Thus, 3-hydroxy-3-*p*-chlorophenyl-1-*p*-nitrophenyltriazenes has been introduced as a new reagent for spectrophotometric determination of V(V).

REFERENCES

1. D.N. Purohit, *Talanta*, **14**, 353 (1967).
2. D. Chakravorty and A.K. Majumdar, *J. Indian Chem. Soc.*, **54**, 258 (1977).
3. R.L. Dutta and S. Ramdhar, *J. Sci. Ind. Res.*, **40**, 715 (1981).
4. D.N. Purohit, A. Nizamuddin and M. Golwalkar, *Anal. Chem.*, **8**, 76 (1985).
5. R. Belcher and C.L. Wilson, *New Methods of Analytical Chemistry*, Chapman & Hall, p. 92 (1964).
6. P. Job, *Ann. Chim.*, **9**, 113 (1928).
7. A.E. Harvey and D.L. Manning, *J. Am. Chem. Soc.*, **72**, 4488 (1950).
8. J.H. Yoe and A.L. Jones, *Ind. Eng. Chem. Anal. Ed.*, **16**, 111 (1944).
9. Y. Zolotov, *Extraction of Chelating Compound*, Ann Arbor, London, p. 136 (1970).
10. A.E. Harvey and D.L. Manning, *J. Am. Chem. Soc.*, **74**, 4744 (1952).