

Spectrophotometric determination of Vanadium with Acetophenone 2', 4'-Dihydroxy Thiosemicarbazone

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Abstract: Acetophenone 2', 4'-Dihydroxy thiosemicarbazone (APDHTS) as a reagent for the extractive spectrophotometric determination of Vanadium¹. The reagent APDHTS gave instantaneous and stable yellow colour with Vanadium (V) at pH 5.2. The colour reaction in detail has been explored and the possibility of photometric determination of the micro amounts of Vanadium is established with necessary conditions². The system obeys Beer's law in the concentration range of 1-10 ppm at 378 nm. A linear calibration graph over the concentration range 1 ppm to 10 ppm with a 3 σ limit of detection of 0.316 ppm was obtained by applying the spectrophotometric method at wavelength 378 nm. The stoichiometry of the complex is established as 1:2 (M:L) by Job's method of continuous variation³ and confirmed by mole ratio method⁴. The standard deviation and the coefficient of variations are presented. The molar absorptivity and Sandell's sensitivity of the complex is 3.4119 x 10³ L mol⁻¹cm⁻¹ and 0.01495 μ g cm⁻² respectively. The results of the prescribed procedure applied for the determination of the micro amounts of V (V) in various synthetic and standard steel samples are presented.

Keywords: Extractive Spectrophotometric Determination, acetophenone 2',4'-dihydroxy thiosemicarbazone (APDHTS), Vanadium, Beer's Law, Molar Absorptivity, Sandell's Sensitivity.

Introduction

Vanadium is found in earth's crust in abundance. It is generally present as Vanadates. The amount of Vanadium in soils and plants has been found to be a critical factor in recent years. The metal is an important alloying element and is present as minor constituent in many industrially important materials. Even small amounts cause tremendous increase in hardness and strength. The increasing use of the metal necessitates development of rapid and sensitive methods for the determination of minute quantities of the metal⁵. Colorimetric and Atomic Emission or Atomic Absorption methods are most commonly used for the determination of Vanadium. However, colorimetric methods are generally preferred; as they involve less expensive instrumentation and afford better sensitivity when appropriate chromogenic reagents and solvent extraction pre-concentration steps are employed. Most of the extractive spectrophotometric methods developed for Vanadium are based on reactions with suitable colour producing reagents⁶ However, most of the existing methods suffer from limitations such as longer periods of time for phase separations⁷⁻⁹, weak stability of coloured complexes and interferences from metal ions like tungsten, tin, antimony and anions and various complexing agents¹⁰. In the present paper, extractive spectrophotometric determination of Vanadium with Acetophenone 2', 4'-dihydroxy thiosemicarbazone (APDHTS) is presented¹¹.

Experimental

Electrochemically and spectrally pure water obtained from triple distillation of deionised feeder water was used for conducting analytical operations. All the chemicals were of Analytical grade quality. The inorganic salt solutions of various metal ions in higher concentrations were prepared by dissolving appropriate salts in requisite quantities in triple distilled water to give a solution containing 100 ppm and few drops of a suitable acid were added before dilution wherever necessary to prevent hydrolysis. A number of buffer solutions¹² of constant ionic strength of 0.2 M covering a wide pH range were prepared. The Ligand APDHTS was synthesized, recrystallized, dried and used for preparing a 0.1% solution in methanol. Solutions of ions for interference studies were prepared by dissolving the amount of each compound needed to give 100 ppm of the ion concerned. All the solutions were stable for several weeks.

Procedure for the Extraction

1.0 mL of aqueous solution containing 1 μ g of Vanadium metal and 1 mL of reagent were mixed in a 50 mL beaker. The pH of the solution adjusted to 5.2 It must be noted that the total volume should not exceed 10 mL. The solution was transferred to 100 mL reparatory funnel. The beaker was washed twice with cyclohexanone and transferred to the same funnel. The two phases were shaken for two minutes and allowed to separate. The organic phase was passed through anhydrous sodium sulphate in order to absorb trace amount of water from organic phase and then collected in 10 mL measuring flask and made up to the mark with organic solvent if required. The amount of Vanadium present in the organic phase determined quantitatively by spectrophotometric method by taking absorbance at 378 nm.

Results and Discussion

The results of various parameters involved during the extraction are discussed below.

Extraction as a function of pH

The optimum pH range in which the metal complex shows maximum and constant absorbance was carried out at different pH range. The extractions were in pH range 4.0 - 6.0 and maximum at 5.2 so for all further extractions the pH was maintained at 5.2 (Fig no.1).

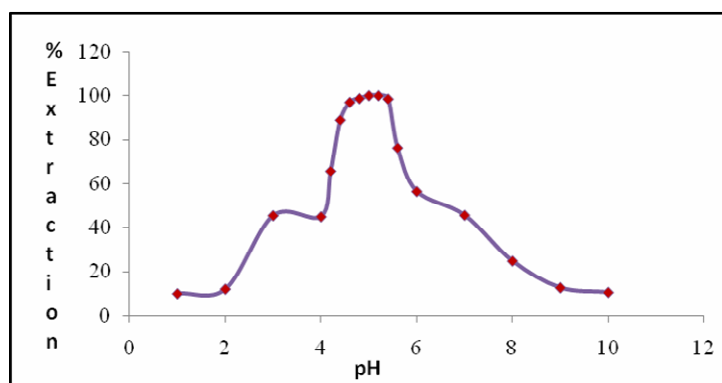


Fig No.1. Effect of pH on the Extraction of V (V)

Absorption Spectrum

The absorption spectra of Acetophenone 2', 4'-dihydroxy thiosemicarbazone (APDHTS), V (V) ion and the V (V)-APDHTS complex in methanolic solution absorbance were recorded from 200-800 nm against reagent blank. From the spectra, the absorption maximum (λ max) of the complex is observed at 378 nm, which is identical for both aqueous and organic phases of the complex, at which, the absorbance of the metal ion and the ligand are negligible or nil. Hence for the spectrophotometric study, all the measurements were carried out at 378 nm. (Fig no.2).

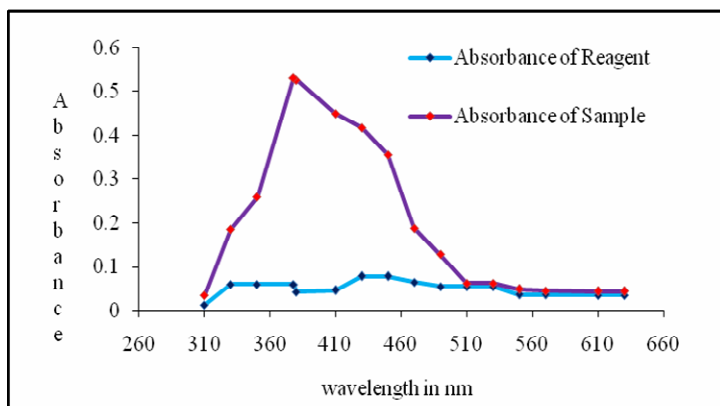


Fig. No. 2. Variation of absorbance with wavelength

Effect of Solvents and Equilibration Time

The absorbance value and the percentage of extraction of V (V)-APDHTS decreased in the order cyclohexanone > benzene > chloroform > carbon tetrachloride > amyl alcohol. It was observed that the extraction was quantitative in 1 minutes of equilibration. Hence to get reproducible results 1 minutes of equilibration was carried out for all extractions.

Effect of Reagent Concentration and Stability of the Complex

The minimum amount of reagent to acquire maximum colour intensity with a given amount of V (V) ion was found that 1ml of the reagent is sufficient for colour development. The absorbance of the complex is uniform even up to 40 hrs.

Applicability of Beer's law

A linear plot was obtained when the measured absorbance values are plotted against the amount of V (V) in the concentration range of 1-10 ppm at 378 nm. The molar absorptivity and Sandell's sensitivity of the complex is $3.4119 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.01495 \mu\text{g cm}^{-2}$ respectively. The composition of the complex responsible for the observed yellow colour in the reaction between the metal ion and the APDHTS is established from the Job's method and mole ratio method was found to be 1:2 (M:L)(Fig no.3).

The Nature of the Extracted Species

The composition of the complex responsible for the observed Lemon Yellow colour in the reaction between the metal ion and the APDHTS is established from the Job's method, mole ratio method and slope ratio method was found to be 1:2 (M:L) (Fig no.4).

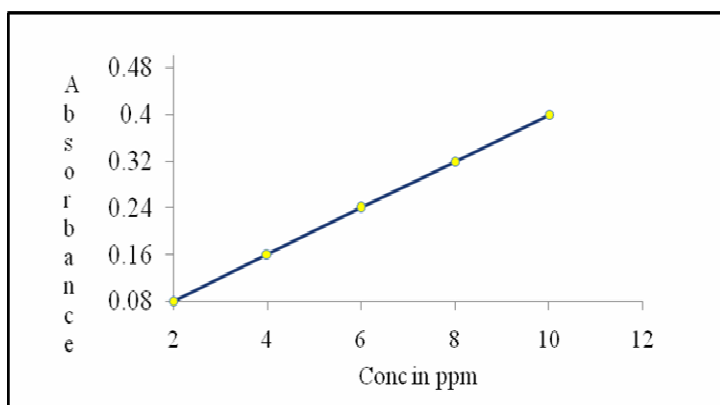


Fig.No.3. Calibration plot

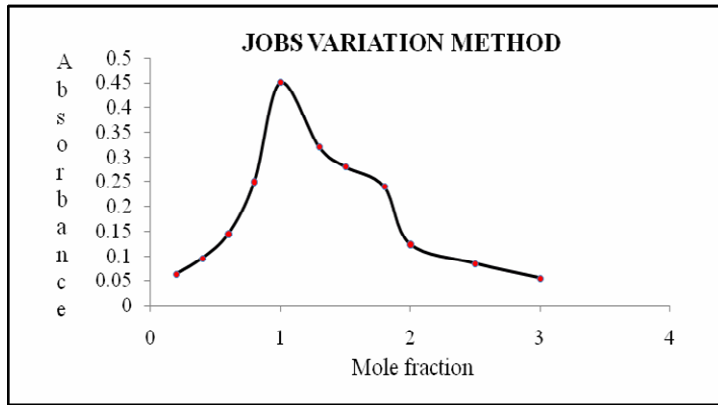


Fig. No.4. Nature of the Extracted species

Effect of divalent ions and foreign ions

The effect of other ions present in various amount indicated no interference in the spectrophotometric determination of 10 ppm of Vanadium. The ions which show interference in the spectrophotometric determination of Vanadium were overcome by using appropriate Masking agents (Table no 1).

Table No 1. Masking Agents Used

Sr. No.	Interfering ion	Masking agent
1	Ni (II)	Sodium cyanide
2	Fe(III)	Sodium Fluoride
3	Cu (II)	Sodium thiosulphate
4	Mo (VI)	Citrate
5	Ag (I)	Potassium iodide
6	U (VI)	8-hydroxy quinoline
7	EDTA	Boiled with concentrated HNO ₃
8	CN ⁻	Boiled with concentrated HNO ₃ and formaldehyde

Precision and Accuracy

The precision and accuracy of the developed spectrophotometric method have been studied by analyzing ten solutions each containing 8 µg of Vanadium in the aqueous phase. The average of ten determinations was 8.0049 and variation from mean at 95% confidence limit was ± 0.0332.

Limit of Detection (LOD)

1 cm³ of 0.1 % methanolic APDHTS is diluted with buffer of pH 5.2 which is then extracted with cyclohexanone as per the procedure and then its absorbance is measured between 378 nm by taking solvent as a blank. The process is repeated for five times separately and five observations are obtained. The limit of detection for Vanadium for the method was found to be 0.316 ppm.

Application

The proposed method was successfully applied for the determination of Vanadium from various alloys, ores and pharmaceutical samples. The results found to be in good agreement with those obtained by the standard known method¹³⁻¹⁴ (Table 2). The developed method is compared with result obtained with the phospho tungstate method for the estimation V (V) and observed to be comparable.

Table No 2. Determination of Vanadium

Synthetic Samples			
Composition of Sample(μg)	Amount of Vanadium (μg)	Standard method	Present method
Zn(4),W(6), Co(8), V(6)	6	5.97	5.8
Zr(5), Ti(2), V(4)	7	6.8	6.67
Steel Alloys			
Carbon steel	6	5.9	5.85
Ferro vanadium	0.5	4.9	4.7

Conclusion

The proposed method permits the determination of trace amounts of vanadium without any prior separation. The major advantage of the proposed method is that the colour development is instantaneous at room temperature and stable. The proposed method has higher sensitivity and selectivity than that of the methods reported earlier.

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References

1. Vogel, A. I., Textbook of Quantitative Inorganic Analysis, 3rd ed., London, (1975).
2. Tomonoki H.A.; Bunseki K.; 29(7) (1980) 472.
3. Simoneko V. I., Soloshonok V.V. and Sukhan V. V.; Zavod. Lab., 58(4) (1992) 4.
4. Desai A. and Naik H.B., J. Ind. Inst. Chem., 64 (3) (1992) 96.
5. Mishra, I. and Mohabey, H.; Bull. Chem. Soc. Japan., 66(5) (1993) 1553
6. Poirier, Jean-Marie and Verchere, Jean-Francois, Talanta, 26 (5) (1979) 341.
7. Roy, A., Roy, S.R. and Chakraborty, A.K.; Glass Technol., 32(1) (1990) 235.
8. Bassett J., Denney R. C., Jeffery G. H., & Mendham J., Textbook of Quantitative Inorganic Analysis, London: ELBS., 4th ed, 1975, 281-287, 337.
9. J. M. Poirier and J. F. Verchere, Talanta, 1979, 26 (5), 341.
10. M.C. Fung and D. L. Bowen, Journal of Toxicology-Clinical toxicology, 1996, 3(4), 119-126.
11. S. Sanjay, American Journal of Medicine, 1998, 1(3), 236-241.
12. Hammond C. R.; The Elements, Handbook of Chemistry and Physics, CRC press, 81st ed., 2000, 224-250.
13. Alan B. G. Lansdown, Silver in healthcare, London, Royal Society of Chemistry., 2010, 5-9.
14. Lokhande R. S., Janwadkar S. P., Kulkarni S. W. and Patil S.K.; Rasayan journal of Chemistry, 2011 4(3), 609-612.
