J. Indian Inst. Sci., 64 (B), May 1983, Pp. 133–136

Short Communication

Spectrophotometric determination of vanadium(V) with salicylaldehyde thiosemicarbazone

N. SUBBA RAMI REDDY AND D. VENKATA REDDY
Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515003, India.

Received on August 17, 1982; Revised on November 29, 1982.

Abstract

Salicylaldehyde thiosemicarbazone forms a yellow-coloured species with vandium(V) at pH 5·0-6·5. A 5-fold excess of the reagent is necesssry for full development of colour intensity. Beer's law is obeyed over the concentration range of 0·5–4·0 ppm. of vanadium(V). The molar absorptivity and Sandell photometric sensitivity at 370 nm are $6 \cdot 30 \times 10^3$ lit. $mole^{-1}$. cm^{-1}. and 8·09 ng. em^{-2} respectively. The composition of the complex established by Job's method is 1 : 1 (metal : ligand). The colour of the complex is found to be stable for over three days. The method is simple, selective, sensitive and needs no extraction or heating.

Key words: Spectrophotometry vanadium(V), salicylaldehyde, thiosemicarbazone.

1. Introduction

Most of the reagents employed for the spectrophotometric determination of vanadium (V) are extractive photometric reagents using non-polar solvents. These reagents suffer from such deficiencies as narrow ranges of determination (0·1–0·5; 0-2·0 ppm), lengthy procedures and interference by common ions[1–4]. Salicylaldehyde thiosemicarbazone (SAT) was employed as an analytical reagent for the gravimetric[5], spectrophotometric[6] and extraction photometric[7] determination of transition metal ions. The colour reaction between vanadium(V) and SAT is utilized for the spectrophotometric determination of vanadium(V). This is the first-ever thiosemicarbazone employed for the spectrophotometric determination of vanadium(V). The present method is simple, selective, sensitive and highly stable and needs no extraction or heating.

2. Experimental

ECIL spectrophotometer model 865 A which is operated in the wavelength region 200–650 nm was used to measure the absorbance. The precision of the instrument at the wavelength of study is ± 0·01 A at 0·4 A. An ELICO Digital pH meter LI-120 was employed for the pH measurements.

The reagent (SAT) was prepared by a refluxing mixture of dilute acetic acid (1·2 N) solution of thiosemicarbazide (4·55 gm) and ethanolic solution (125 ml) containing 6·1 gm of salicylaldehyde on a water bath (100° C) for 30 minutes[8]. The contents were later cooled and the solid separated was filtered, dried and recystallized from 60% aqueous ethanol (m.p. 235° C). The reagent solution was prepared in methanol.

The stock solution of vanadium(V) was prepared from ammonium meta vanadate and the solution was standardised by iodometric method reported by Vogel[9]. All the chemicals used were AnalaR Grade.

3. Results and discussion

Vanadium(V) reacts with salicylaldehyde thiosemicarbazone in the pH range 1-10 to give an yellow solution with an absorption maximum at 370 nm. The absorbance at 370 nm is highest in the pH range 5·0–6·5 (Fig. 1) and a 5-fold excess of the reagent is necessary for full colour development. The absorbances at 370 nm of the complex and the reagent at different pHs are presented in fig. 2. Requisite volume of

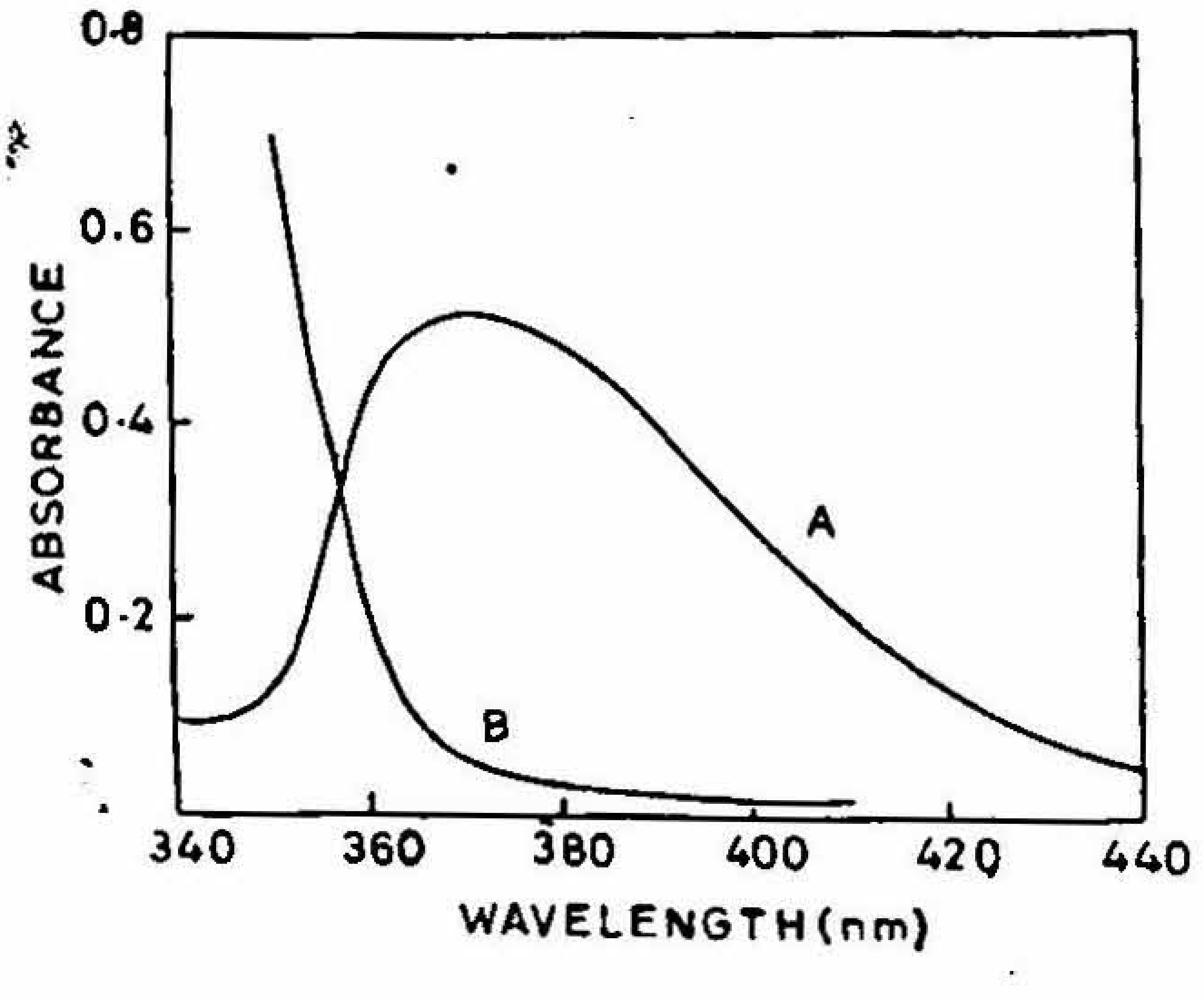


Fig. 1. Absorption spectra
A : V (V)-SAT complex against reagent blank.
B : Reagent blank against MeOH (aq)
[V(V)] = 8 × 10^{-5} M
[SAT] = 4 × 10^{-4} M

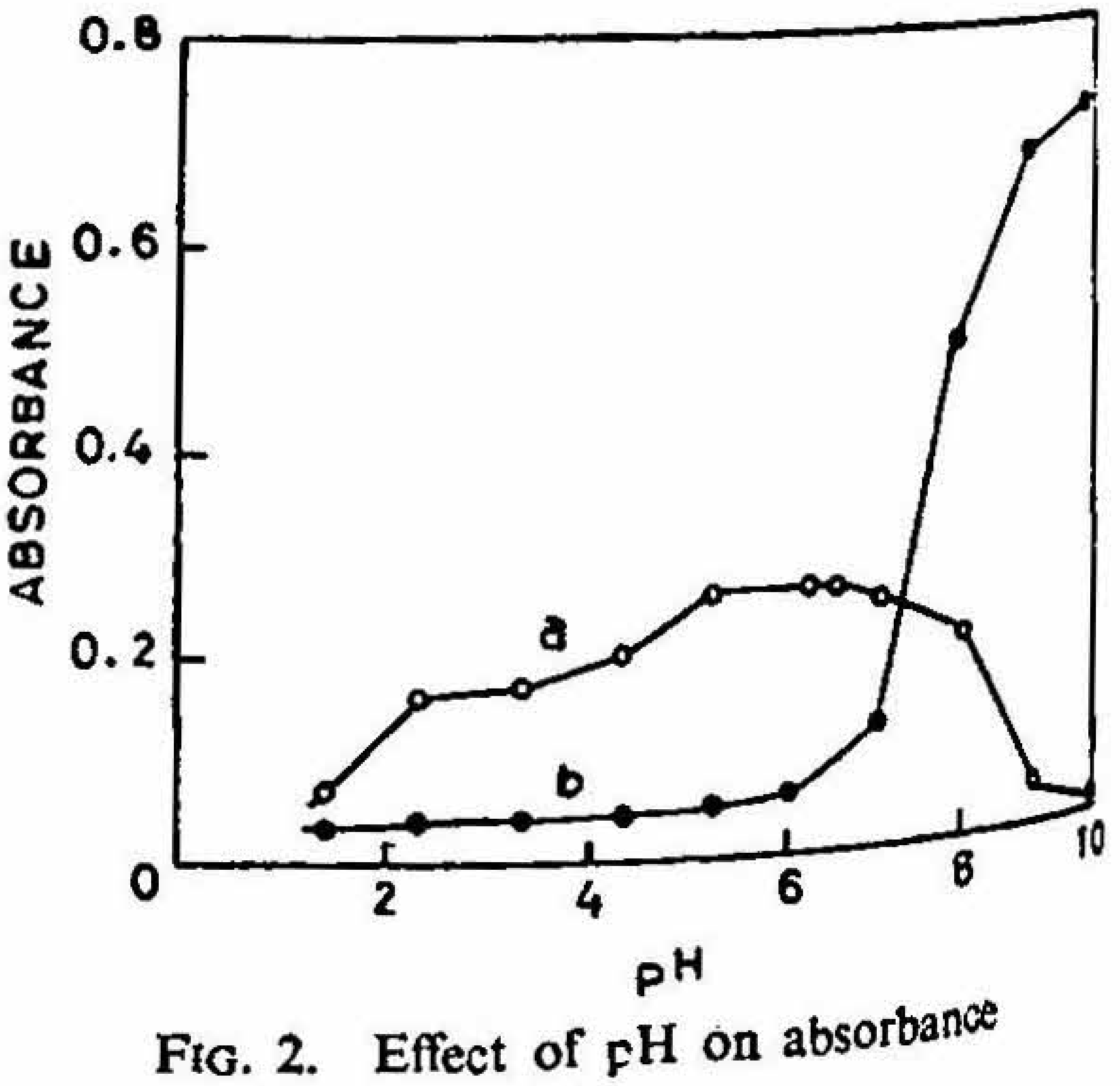
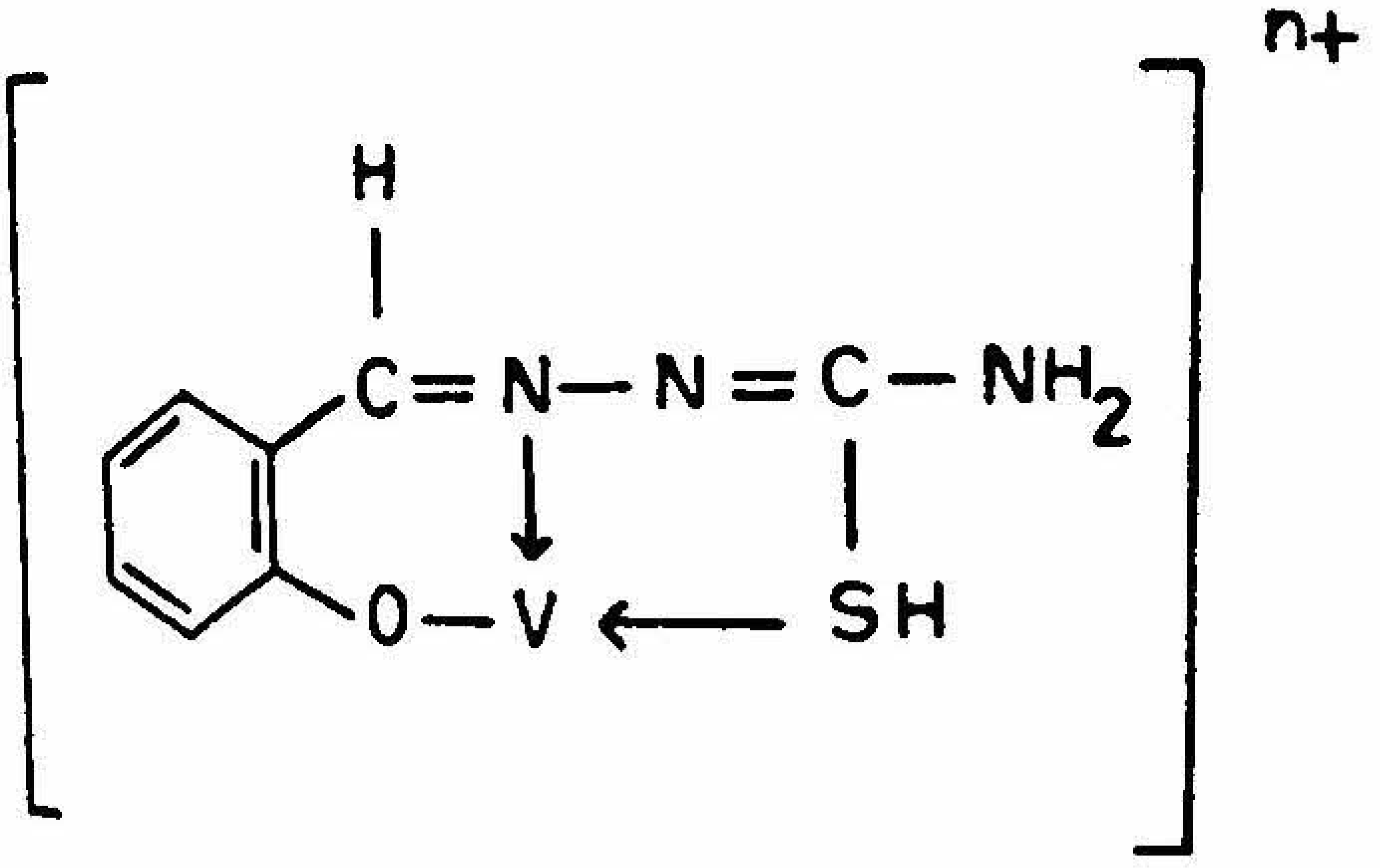


Fig. 2. Effect of pH on absorbance
A : V-SAT complex
B : Reagent blank
[V (V)] = 4 × 10^{-5} M
[SAT] = 4 × 10^{-4} M

methanol is added to avoid precipitation of the reagent. Colour formation is instantaneous and the order of addition of the components has no effect on the absorbance. However, methanol has to be added before the addition of the reagent. Beer's law is obeyed in the range 0·5–4·0 ppm of V(V). The optimum range for effective spectrophotometric determination of vanadium determined by Ringbom plot is 1·5–4·0 ppm. The molar absorptivity and Sandell photometric sensitivity are $6 \cdot 30 \times 10^3$ lit. $mole^{-1}\,cm^{-1}$ and 8·09 ng. cm^{-2} respectively. The relative deviation in the absorbance is 1·24% when the measurements are made at 4 ppm V(V).

The composition of the complex was determined by Job's method of continuous variation and the mole ratio method and is found to be 1 : 1 (metal : ligand). The structure of the complex is proposed as



The stability constant of the complex was calculated from the data of Job's curve utilizing the equation.

$$\beta = \frac{A/A_m}{(1 - A/A_m)^2 \cdot C}.$$

The stability constant is $2 \cdot 1 \times 10^5$.

3.1. *Recommended procedure*

Transfer a suitable aliquot containing 12·5–100 μg vanadium(V) solution into a 25 ml volumetric flask. Add 12 ml of sodium acetate-acetic acid buffer solution (pH 6·0), 4 ml of methanol and 1 ml of 0·01M reagent solution. Shake the contents and dilute the same to mark with water. Measure the absorbance in 1 cm cells at 370 nm against the reagent bank,

3.2. *Effect of various ions*

The effect of foreign ions on the colour reaction is studied in the determination of 4 ppm of V(V). A deviation of ± 2% in the absorbance reading was considered tolerable.

Hundred-fold excess of Fe(II), Mn(II), Mo(VI), fluoride, thiocyanate and 200-fold excess of phosphate, citrate and tartrate are tolerated. Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) interfere through the formation of coloured complexes with the reagent. Interference of iron(III) is eliminated by separating it as iron(III)-phosphate. Copper(II) and nickel(II) are masked with sodium thiosulphate and tri-ammonium citrate respectively. Chromium(III) and vanadium(IV) interfere by their colour. Cd(II), Ag(I) and Pd(II) interfere through the formation of coloured precipitates with the reagent.

Acknowledgement

Authors are thankful to Prof. S. Brahmaji Rao, Head of the Department of Chemistry, for useful discussions. N.S.R. is grateful to CSIR, New Delhi, for the award of Post-Doctoral Fellowship. Thanks are due to the authorities of Sri Krishnadevaraya University for providing facilities.

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