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ORIGINAL ARTICLE

Catalytic and kinetic spectrophotometric method for determination of vanadium(V) by 2,3,4-trihydroxyacetophenonephenylhydrazone



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samples

Abstract A new catalytic and kinetic spectrophotometric method for the determination of vanadium(V) was studied using 2,3,4-trihydroxyacetophenonephenylhydrazone (THAPPH) as an analytical reagent. The present method was developed on the catalytic effect of vanadium on oxidation of THAPPH by hydrogen peroxide in hydrochloric acid–potassium chloride buffer (pH = 2.8) at the 20th minute. The metal ion has formed 1:2 (M:L) complex with THAPPH. Beer's law was obeyed in the range 20–120 ng/mL of V(V) at λ_{\max} 390 nm. The sensitivity of the method was calculated in terms of molar absorptivity ($1.999 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$) and Sandell's sensitivity ($0.000254 \mu\text{g cm}^{-2}$), shows that this method is more sensitive. The standard deviation (0.0022), relative standard deviation (0.56%), confidence limit (± 0.0015) and standard error (0.0007) revealed that the developed method has more precision and accuracy. The stability constant was calculated with the help of Asmu's (9.411×10^{-11}) and Edmond's & Birnbaum's (9.504×10^{-11}) methods at room temperature. The interfering effect of various cations and anions was also studied. The present method was successfully applied for the determination of vanadium(V) in environmental and alloy samples. The method's validity was checked by comparing the results obtained with atomic-absorption spectrophotometry and also by evaluation of results using F-test.

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1. Introduction

Vanadium comprises about 0.02% of earth's crust (Beusen and Neven, 1987). It is a metallic element abundantly distributed in nature and it is an essential element for plants in vestigial amounts. In plants and microorganisms, vanadium is not only helpful for cell growth but also plays a key role in nitrogen

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fixation and accumulation (Mukherjee et al., 2004). In large amounts vanadium can become a relatively toxic element, depending on its oxidation state. In aqueous environments vanadium(V) is more toxic than vanadium(IV). Vanadium poisoning leads to nervous depression, coughing, vomiting, diarrhea, anemia and increased risk of lung cancer. Bronchitis and bronchopneumonia as well as irritation of eyes and skin can occur due to occupational exposure to airborne vanadium (Klaassen, 2008). The utilization of vanadium and its compounds in steel and petrochemical industries has resulted in the release of large amounts of vanadium compounds to air, water and soil. The control of vanadium content, especially V(V), in waste waters and environmental samples from highly polluted areas became an alarming issue (Pyrzynska and Wierzbicki, 2004). Hydrazones are important class of known analytical reagents for detection and determination of metal ions. The potential analytical applications of hydrazones derivatives have been reviewed (Srilalitha et al., 2010).

The survey of literature reveals that several procedures have been reported for the determination of vanadium. The procedures include high performance liquid chromatography (HPLC) (Vachirapatama et al., 2002), electrochemical (Ensafia and Naderi, 1997), spectrofluorimetry (Pei-hong et al., 2010), neutron activation analysis (Kawakubo et al., 1995a,b), atomic-absorption spectroscopy (Greenberg and Kingston, 1983), ion chromatography inductively coupled plasma optical emission spectrometry (Tatsuya et al., 1999), spectrophotometry (Coetzee et al., 2002; Pyrzynska, 2005; Gavazov et al., 2006), etc. These techniques are not only sensitive, inconvenient, expensive and time consuming but also very complicated (Jianbo Liu et al., 2009). These techniques involve preliminary isolation and pre-concentration procedures. Several kinetic methods based on its catalytic action on the oxidation of organic compounds have also been reported in literature (Richard et al., 1995; Kawakubo et al., 1995a,b; Mohamad and Fawy, 2000; Shigenori et al., 2005; Hu et al., 2004).

Thus, highly sensitive and selective methods are still required for tracing vanadium determination in different kinds of samples. In the present work a simple, rapid, sensitive and selective kinetic spectrophotometric method is studied and has been successfully applied for the determination of vanadium in soil samples, tobacco leaf samples, water samples and alloy samples using a new reagent 2,3,4-trihydroxyacetophenonephenylhydrazone (THAPPH). The proposed method when compared to other spectrophotometric methods Table 1 is found to be more sensitive and selective.

2. Experimental

2.1. Physical measurements

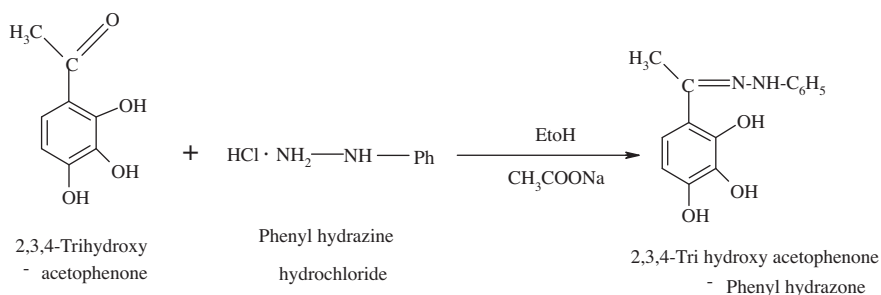
Determination of metal ion concentration was carried out by a Shimadzu 2450 UV-VIS spectrophotometer equipped with 1.0 cm quartz cell and the pH of the solution was tested with an Elico Li-120 digital pH meter. A Perkin-Elmer 170-30 atomic-absorption spectrophotometer was used for the comparison of results.

2.2. Synthesis of the ligand

2,3,4-Trihydroxyacetophenonephenylhydrazone (THAPPH) (Scheme 1) was prepared by dissolving accurately weighed 2.5 g of phenylhydrazine hydrochloride and 3.0 g of sodium acetate in 100 mL of double distilled water. An alcoholic solution of 2,3,4-trihydroxyacetophenone (1.6 g) is added to the above solution and the mixture was heated on a hot water bath for about 30 min and was kept overnight. The pale yellow colored product of 2,3,4-trihydroxyacetophenonephenylhydrazone (THAPPH) obtained was filtered and recrystallised using 30% ethanol in the presence of animal charcoal. The purity of the reagent was checked by melting point (m.p. 146–147 °C) and TLC. Spectral characterization of 2,3,4-tri-

Table 1 Comparison of the present method with other spectrophotometric methods for the determination of vanadium(V).

Reagent	λ_{\max}	pH/medium	Beer's law range (ppm)	Molar absorptivities (ϵ) $\times 10^4$	Reference
Pyrogallol	580	6.0	0–14	0.775	Iranpur et al. (1992)
Thiosalicylic acid	600	Monochloro acetic acid	0–3	0.17	Salinas et al. (1992)
3-Hydroxy-3-phenyl- <i>p</i> -carboxyphenyltriazone	395	6.5–7.0	0.5–3.5	0.955	Razie et al. (1994)
2,2'-Iminodibenzoic acid	610	Monochloro acetic acid	0.4–20	1.2	Zhou et al. (1994)
5-Aminoindazol-zodyes	–	–	1–2	0.58	Mustafa et al. (1995)
<i>N</i> -phenyl cinnamohydroxamic acid	530	3–10 M – chloroacetic acid	0.5–10	0.67	Abebaw and Chandravanshi (1996)
4-Benzol-3-methyl-1-phenyl pyrazole-5-one	480	–	120	0.0625	Bieluonwu (1996)
2,4-Dihydroxy acetophenone benzoyl hydrazone	275	–	Up to 7.2	1.25	Sharma and Mehtha (1996)
5,7-Dibromo-8-hydroxyquinoline	420	–	0–4	0.727	Arya and Mahajan (1997)
Thionin	600	Acid medium	0.2–10.0	2.298	Tom and Narayana (2005)
3,4-Dihydroxy benzaldehyde isonicotinoylhydrazone	360	5.5	0.5–5.3	1.29	LakshmiNarayana et al. (2008)
Salicylaldehydeacetoacetic acid hydrazone	460	2	0.2432–0.438	2.2	Srilalitha et al. (2010)
2,3,4-Trihydroxy acetophenone phenyl hydrazone (THAPPH)	390	2.8	0.02–0.16	19.99	Present method



Scheme 1 Preparation of 2,3,4-trihydroxyacetophenonephenylhydrazone (THAPPH).

hydroxyacetophenonephenylhydrazone: IR data (KBr cm^{-1}): 3490 $\nu(\text{O-H})$, 3287 $\nu(\text{N-H})$, 1638 $\nu(\text{C} = \text{N})$, LC-MS data: $[\text{M} + \text{H}]^+ = 259$, $^1\text{H-NMR}$ data(CDCl_3 δ ppm): 2.1(3H, CH_3), 5.9(1H, NH), 6.7–7.3(7H, ArH), 7.5–7.8(3H, OH). The spectra of IR, LC-MS and $^1\text{H-NMR}$ are shown in Figs. 1–3, respectively.

2.3. Preparation of a stock solution vanadium(V)

0.0196 M vanadium(V) solution is prepared by dissolving 0.2296 g of ammonium metavanadate (NH_4VO_3) in hot distilled water. The solution is later cooled, diluted to 100 mL and standardized using a standard solution of ferrous ammonium sulfate.

2.4. Buffer solution

0.1M hydrochloric acid and 0.1M potassium chloride solutions are prepared in distilled water and suitable portions

of these solutions are mixed to get the desired pH using a pH meter.

2.5. Recommended procedure

An aliquot of metal ion solution, 5.0 mL of hydrochloric acid–potassium chloride buffer solution (pH = 2.8), 4.0 mL of THAPPH solution (1.0×10^{-4} M) and 1.0 mL of 0.03% v/v hydrogen peroxide solutions were taken in a 25.0 mL standard flask and the contents were made upto the mark with distilled water. The absorbance of the solution is recorded at 390 nm, against the reagent blank, at the 20th minute.

2.6. Soil samples

An air dried homogenized soil sample (1.0 g) was weighed accurately and placed in a 100 mL Kjeldahl flask. The samples were digested in the presence of an oxidizing agent by Jackson's (1987) method. The contents in flask were filtered

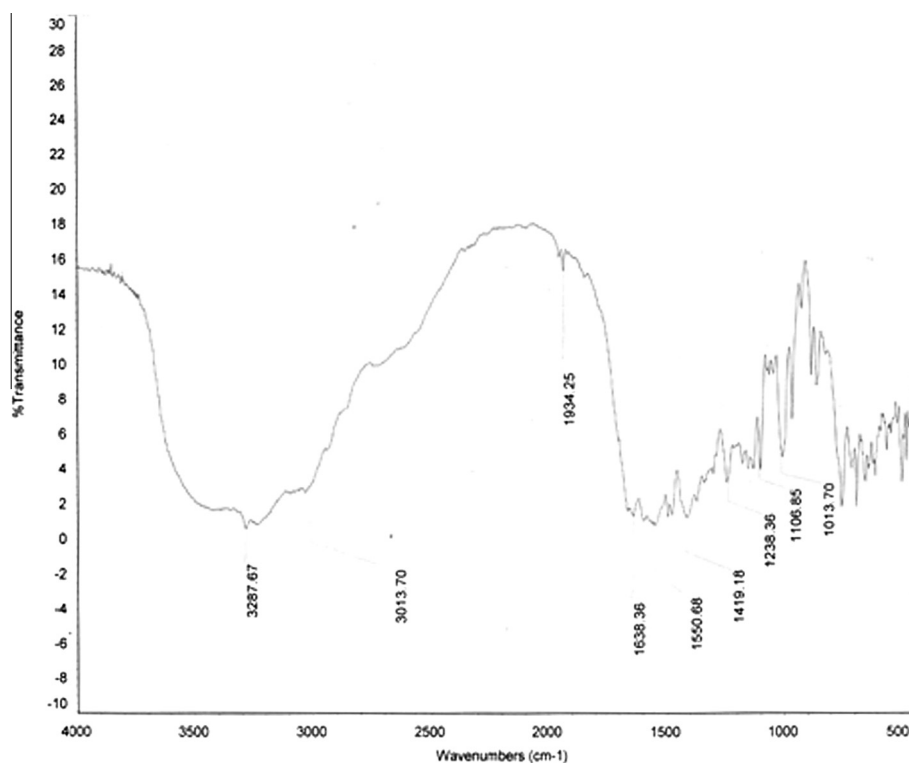


Figure 1 IR spectrum of the 2,3,4-trihydroxyacetophenonephenylhydrazone (THAPPH).

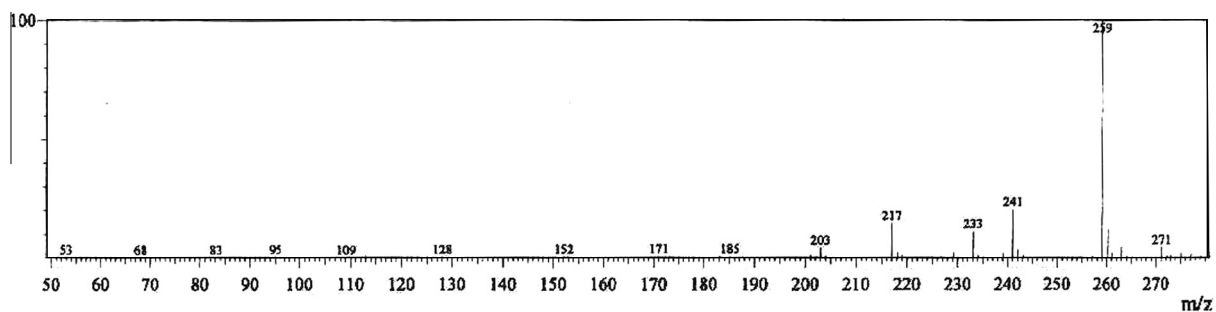


Figure 2 Mass spectrum of the 2,3,4-trihydroxyacetophenonephenylhydrazone (THAPPH).

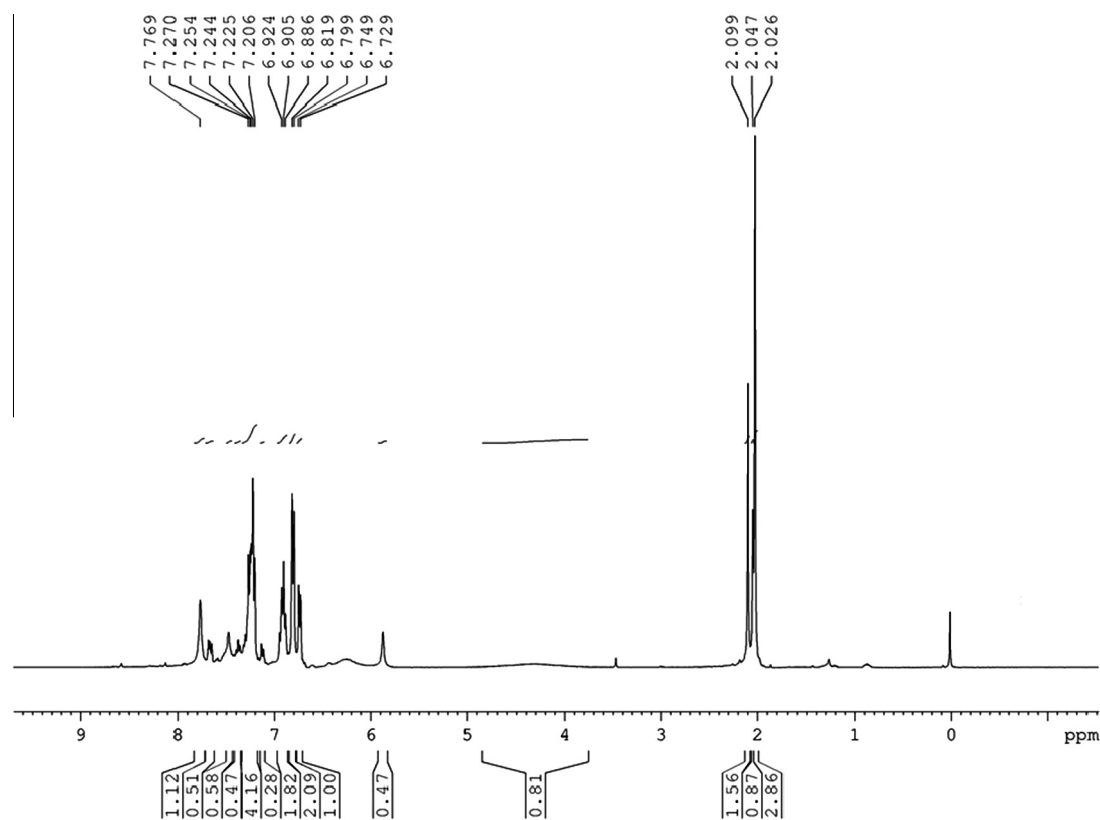


Figure 3 $^1\text{H-NMR}$ spectrum of the 2,3,4-trihydroxyacetophenonephenylhydrazone (THAPPH).

through a Whatmann No. 41 filter paper and neutralized with ammonia. Appropriate aliquot of the solution was transferred into a 25.0 mL standard flask and analyzed for vanadium content according to the recommended procedure.

2.7. Tobacco leaf samples

The tobacco leaves were dried over $110\text{ }^\circ\text{C}$ and grinded. This powder was taken in a 100 mL standard flask and digested with conc. H_2SO_4 . Suitable volumes of the sample were used for the analysis of vanadium(V) as mentioned in the recommended procedure (Kiran Kumar and Revanasiddappa, 2005).

2.8. Water samples

Each filtered environmental water sample (100 mL) was analyzed for vanadium and they were tested negative. Different synthetic samples were prepared with the metal ions which are commonly associated with vanadium(V) and known amounts of vanadium(V). These samples were analyzed for vanadium(V) by the recommended procedure (Kiran Kumar and Revanasiddappa, 2005).

2.9. Alloy samples

About 100 mg of alloy sample (BCS-CRM 485) was dissolved in 15.0 mL of aquaregia, heated to near dryness and the nitrate

was expelled from the residue, using 5.0 mL of conc. HCl. This residue was extracted into double distilled water and made up to the mark of 100 mL standard flask. Suitable volume of this solution was taken and used for the analysis of vanadium(V) as mentioned in the recommended procedure (Kiran Kumar and Revasiddappa, 2005).

3. Results and discussion

The rate of catalyzed oxidation of THAPPH can be influenced by pH of the solution, concentration of the reagent, presence of hydrogen peroxide, temperature of the system and foreign ions associated with it. Hence the above factors are studied in detail to establish suitable conditions for higher sensitivity and selectivity in its determination.

3.1. Absorption spectra of the reagent and complex

An aliquot of 2.0 mL of 1.9630×10^{-5} M vanadium(V) solution is transferred into a 25 mL standard flask. To it, 4.0 mL of 1.0×10^{-4} M 2,3,4-trihydroxy acetophenone phenylhydrazone (i.e. 5-fold excess), 1.0 mL of 0.3% v/v hydrogen peroxide and 5.0 mL of pH 2.8 hydrochloric acid–potassium chloride buffer are added. The solution is made up to the mark of the flask with distilled water. Then the spectrum of the complex is recorded against the reagent blank. Similarly, the absorption spectrum of the reagent is also recorded using distilled water as blank. The spectrum is shown in Fig. 4. The complex has λ_{\max} at 390 nm and the reagent shows minimum absorption at this wavelength and hence is not interfering in the determination. Therefore, further measurements are made at 390 nm.

3.2. Effect of pH

To study the effect of pH, hydrochloric acid–potassium chloride buffer solutions are used for pH values from 1.0–3.2 and sodium acetate–acetic acid buffer solutions are used for

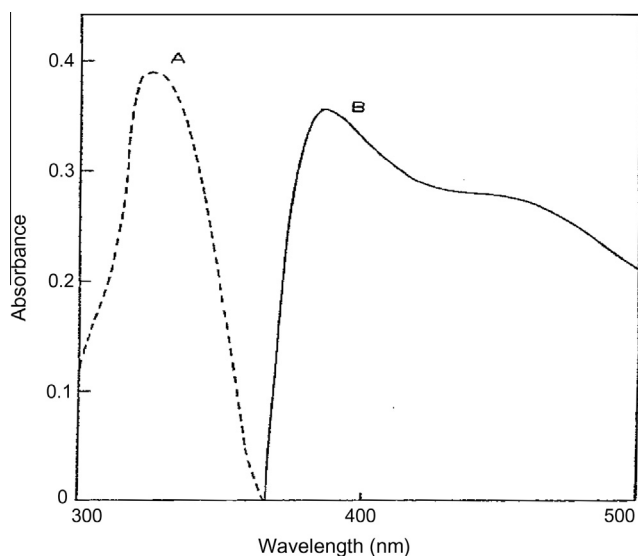


Figure 4 (A) Absorbance spectrum of the reagent and (B) absorbance spectrum of V(V)–THAPPH complex.

pH values from 3.4–4.0. Different aliquots containing 2.0 mL of 1.9630×10^{-5} M vanadium(V), 4.0 mL of 1.0×10^{-4} M reagent and 1.0 mL of 0.3% v/v hydrogen peroxide solutions are prepared in 25 mL standard flasks. To these solutions, 5.0 mL of suitable buffer solutions (pH 1.0–4.0) are added. These solutions are made up to the mark with distilled water and the absorbances are measured at 390 nm (at the 20th minute). A plot (Fig. 5) drawn between pH and absorbance shows that the absorbance is maximum at pH 2.8. Hence, further studies are made at pH 2.8.

3.3. Effect of hydrogen peroxide

To study the effect of hydrogen peroxide, different solutions containing same volumes of vanadium(V), buffer and reagent solutions are prepared. To these solutions 1.0 mL of H_2O_2

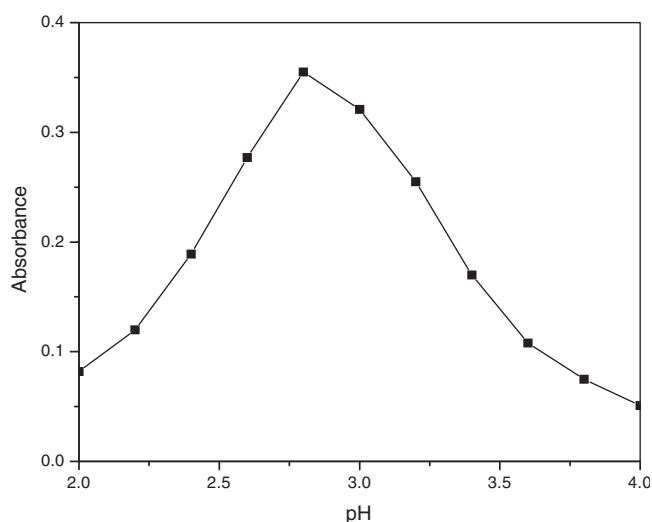


Figure 5 Effect of pH on absorbance of V(V)–THAPPH complex.

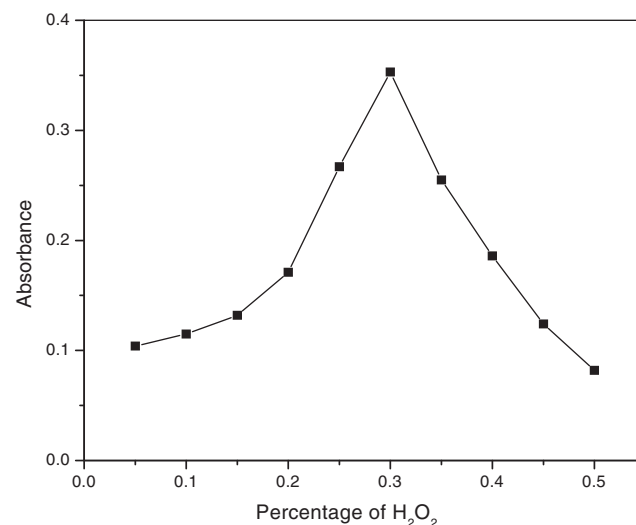


Figure 6 Effect of H_2O_2 on absorbance of V(V)–THAPPH complex.

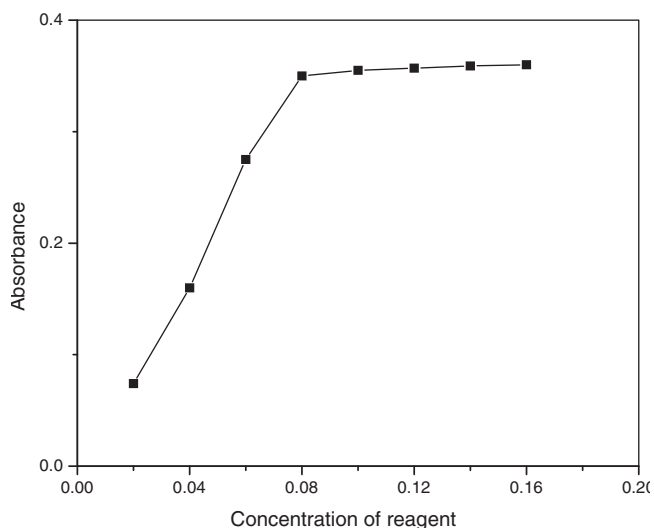


Figure 7 Effect of reagent concentration on absorbance of V(V)-THAPPH complex.

solution of suitable concentration from 0.05% to 0.5% are added and finally the volumes are adjusted to 25 mL. The absorbance of the colored solutions is measured at 390 nm at the 20th minute. The experiment are carried out by fixed time method. The catalyzed oxidation is slow below 0.3% v/v of hydrogen peroxide, as shown in (Fig. 6). Further increase in the concentration of hydrogen peroxide reduces the absorbance. The maximum absorption is at 0.3% v/v hydrogen peroxide. Hence, further studies are carried out by employing 0.3% v/v hydrogen peroxide solution.

3.4. Effect of reagent concentration

The intensity of the color varies with the concentration of THAPPH in the reaction mixture. Hence it is necessary to fix the optimum concentration of the reagent required in the investigation. To study the effect of the reagent concentration,

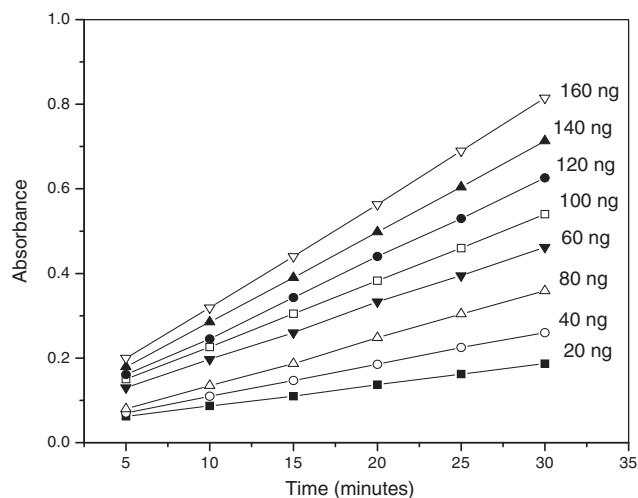


Figure 8 Variation of absorbance with time for different concentrations of vanadium(V).

different solutions are prepared by mixing constant volumes of all the solutions, except the reagent solution. To these solutions varying volumes (0.5–4.0 mL) of 1.0×10^{-4} M reagent solution are added and the total volume is adjusted to 25 mL. Absorbance values are recorded in each case at 390 nm (at the 20th minute). It is found that the absorbance increases up to 5-fold excess of the reagent. There is no increase in the rate of oxidation when the concentration of the reagent is more than 5-fold excess. From the above experiment it is clear that the addition of 5-fold molar excess of the reagent solution is necessary for the maximum color development (Fig. 7).

3.5. Applicability of the method

To different aliquots of solutions containing varying amounts of vanadium(V) solution (20–160 ng/mL) in 25 mL standard flasks, 5.0 mL of hydrochloric acid-potassium chloride buffer

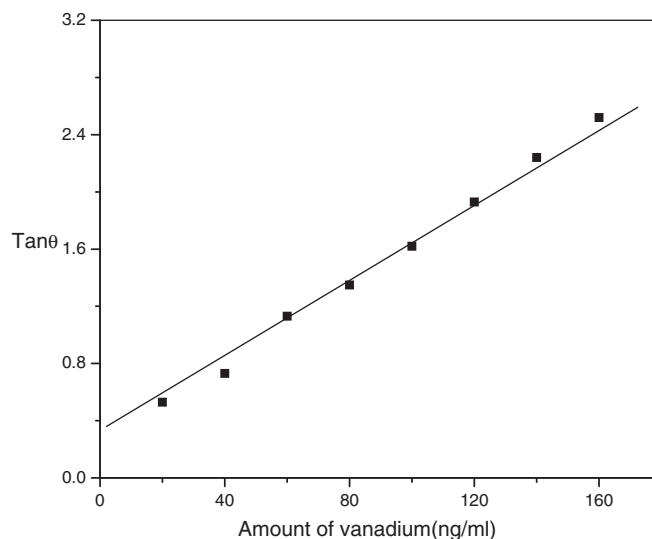


Figure 9 Calibration curve for the determination of by vanadium(V) by tangents method.

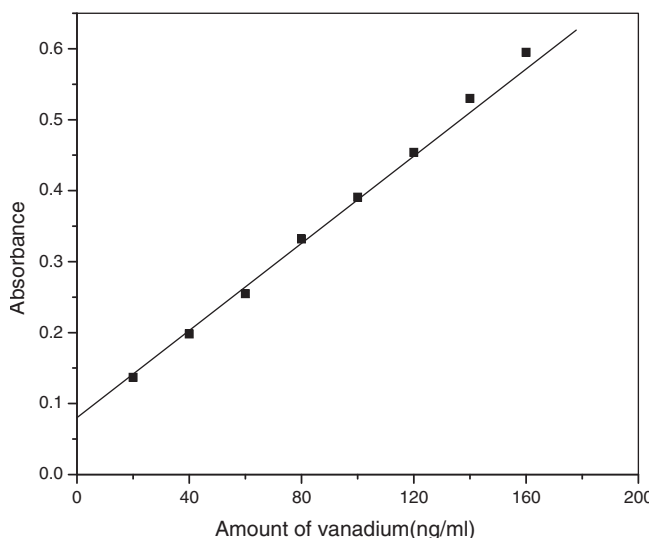


Figure 10 Calibration curve for the determination of vanadium(V) by fixed time method.

(pH 2.8), 4.0 mL of 1.0×10^{-4} M reagent and 1.0 mL of 0.3% v/v hydrogen peroxide solutions are added. These solutions are made up to the mark and the absorbances are measured for every 5 min, using a reagent blank of the same concentration, at 390 nm. The results are shown in Fig. 8. The rate of the catalyzed reaction increases with increase in the concentration of vanadium. Slope values ($\tan \theta$) are calculated for each curve and a graph plotted between $\tan \theta$ and concentration shows a straight line in the range of 20–120 ng/mL of vanadium (Fig. 9). The determination is also carried out using fixed time method. The plot is drawn between the amount of vanadium(V) and its absorbance (Fig. 10). In this method also, the determination range of vanadium(V) is 20–120 ng/mL and is in conformity with the tangents method.

3.6. Sensitivity, precision and accuracy of the method

The molar absorptivity of the V(V)-THAPPH complex is $1.999 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. The Sandell's sensitivity of the complex is $0.000254 \mu\text{g cm}^{-2}$. These values reveal that the method

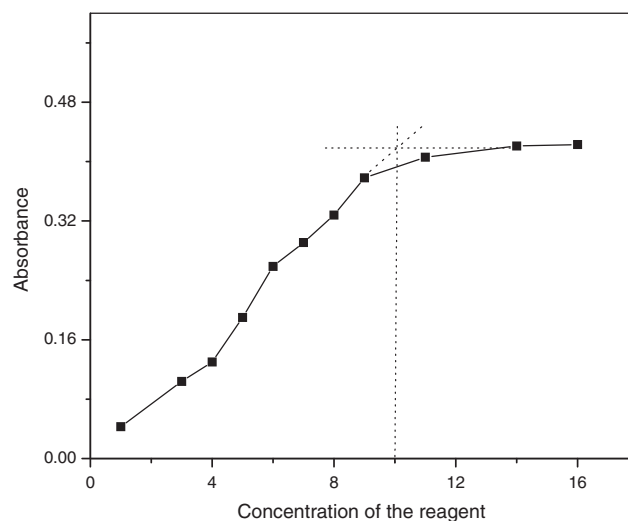


Figure 12 Molar ratio method for determination of composition of V(V)-THAPPH complex.

is sensitive. The standard deviation (0.0022), relative standard deviation (0.56%), confidence limit (± 0.0015) and standard error (0.0007) values show that the precision and accuracy of the method is good.

3.7. Effect of temperature

The effect of temperature is studied by warming a reaction mixture containing 2.0 mL of 1.9630×10^{-5} M vanadium(V), 5.0 mL of pH 2.8 buffer, 4.0 mL of 1.0×10^{-4} M reagent and 1.0 mL of 0.3% v/v hydrogen peroxide solutions on a water bath at 60 °C. The absorbance values (20th minute) at 30 and 60 °C are 0.354 and 0.357, respectively. As there is no significant change in absorbance with temperature, the reaction is carried out at room temperature only.

3.8. Composition of the complex

The composition of the complex is arrived at by Job's continuous variation, molar ratio and Asmus' methods.

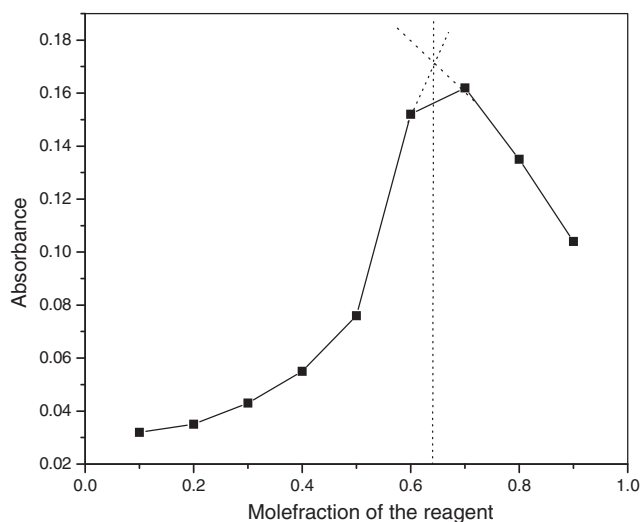


Figure 11 Job's method of continuous variation for the determination of composition of V(V)-THAPPH complex.

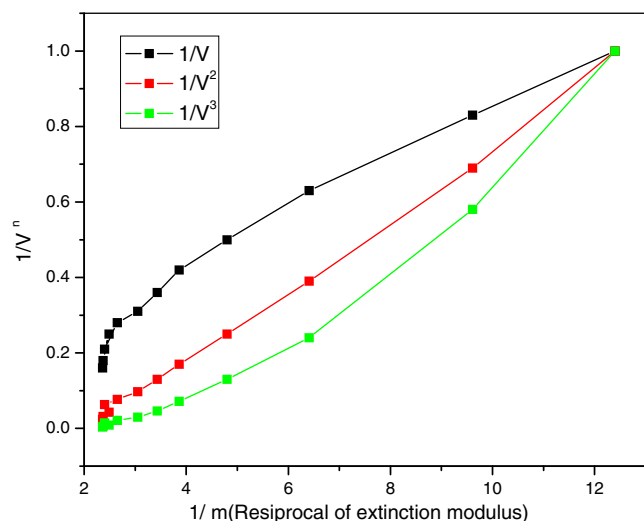


Figure 13 Asmus' method for the determination of composition of V(V)-THAPPH complex.

3.8.1. Job's method of continuous variation

The concentrations of both vanadium(V) and THAPPH solutions are maintained at 1.9630×10^{-4} M in determining the composition of the complex by this method (Job, 1928). A series of solutions are prepared by mixing 'X' mL of THAPPH with (1-X) mL of vanadium(V) solution ('X' is varied from 0.1 to 0.9 mL). In all cases, 5.0 mL of hydrochloric acid-potassium chloride buffer (pH 2.8) and 1.0 mL of 0.3% v/v hydrogen peroxide solutions are added. The solutions are made upto 25 mL with distilled water. Each of the absorbance measurements are made at 390 nm, against the reagent blank, at the 20th minute. The plot is drawn between absorbance and mole fraction of the reagent (Fig. 11). From the plot, it is observed that vanadium(V) to THAPPH ratio in the complex is 1:2.

3.8.2. Molar ratio method

2.0 mL of 1.0×10^{-4} M vanadium(V) solution in different 25 mL standard flasks are treated with different volumes (1-16 mL) of 1.0×10^{-4} M reagent solution. In all the cases, 5.0 mL of pH 2.8 buffer and 1 mL of 0.3% v/v hydrogen peroxide solutions are added, finally the solutions are made up to the mark with distilled water. The absorbance measurements are made at 390 nm against the reagent blank, at the 20th minute. The graph is drawn between the concentration of the reagent and its absorbance (Fig. 12). The graph has revealed that the metal to ligand ratio in the complex is 1:2.

3.8.3. Asmus' method (Asmus, 1960)

To different 5.0 mL vanadium(V) solutions of concentration 1.0×10^{-4} M, varying volumes (1.0-6.4 mL) of 1.0×10^{-4} M reagent solution are mixed. To these solutions, 5.0 mL hydrochloric acid-potassium chloride buffer (pH 2.8) and 1.0 mL of 0.3% v/v hydrogen peroxide solutions are added and the contents of flasks (25 mL) are made up to the mark with distilled water. Each of the absorbance measurements are made at 390 nm against the reagent blank at the 20th minute along with $1/v$, $1/v^2$, $1/v^3$ values and $1/m$, where 'm' is the extinction modulus. Extinction modulus is calculated by dividing the absorbance of the cell width which is 1 cm. A linear plot is obtained when a curve is drawn between $1/v^2$ vs $1/m$. This linear plot (Fig. 13) proved that the metal to ligand ratio in the complex is 1:2. This ratio is in conformity with the ratios of Job's method of continuous variation and molar ratio method.

3.9. Instability constant of vanadium(V)-2,3,4-trihydroxyacetophenone phenylhydrazone complex

3.9.1. Asmus' method

The instability constant is calculated from the data obtained in (Table 2). From the intercept on x-axis of Fig. 10, the instability constant of the complex is calculated by making use of the following equation:

$$\text{Intercept} = -(bo/v)^n \cdot 1/k$$

Here the value of 'n' is 2 and the intercept obtained from graph is -0.170. 'k' value obtained after substitution of these values in the above equation is 9.411×10^{-11} at 30 °C.

3.10. Edmonds and Birnbaum's method

Absorbance of solutions containing the fixed amount of vanadium(V) (8×10^{-6} M) but different known amount ($0.48-1.28 \times 10^{-5}$ M) of reagent solutions are measured after making up the volume to 25 mL, keeping other parameters constant. In each case the reagent concentration is always in excess of the metal ion. The absorbances are measured at 390 nm against the reagent blank and the data are recorded in (Table 2). The instability constants are calculated by choosing different pairs of solutions. The instability constant of the complex is found to be 9.504×10^{-11} at 30 °C.

3.11. Effect of foreign Ions

The effect of various foreign ions on the absorbance of V(V)-THAPPH complex is investigated. To various mixtures containing 2.5 mL of vanadium(V), 4.0 mL of 1.0×10^{-4} M

Table 2 Instability constant by Edmonds and Birnbaum's method: concentration of V(V) solution = 8.0×10^{-6} M.

Concentration of THAPPH $\times 10^{-5}$ M	Absorbance	Instability constants in pairs $\times 10^{-11}$
0.48	0.104	1 & 2 = 7.370 2 & 3 = 9.310
0.64	0.156	1 & 3 = 8.220 2 & 4 = 10.317
0.80	0.208	1 & 4 = 9.098 2 & 5 = 9.785
0.96	0.259	1 & 5 = 8.992 2 & 6 = 10.710
1.12	0.297	1 & 6 = 9.742
1.28	0.341	Average value = 9.504×10^{-11} at 30 °C

Table 3 Effect of foreign ions: amount of vanadium(V) = 0.1 µg/mL.

Foreign ion	Added salt formula	Tolerance limit (µg/mL)
Ag(I)	AgNO ₃	0.5
Al(III)	Al(NH ₄)(SO ₄) ₂ ·12H ₂ O	0.5
Be(II)	BeSO ₄ ·4H ₂ O	1.0
Bi(III)	Bi(NO ₃) ₃ ·5H ₂ O	None
Ca(II)	CaCl ₂	5.0
Cd(II)	(CH ₃ COO) ₂ Cd·2H ₂ O	5.0
Co(II)	CoCl ₂ ·7H ₂ O	10.0
Cu(II)	CuSO ₄ ·5H ₂ O	1.0
Cr(III)	Cr ₂ (SO ₄) ₃	None
Cr(VI)	K ₂ Cr ₂ O ₇	None
Fe(II)	(NH ₄) ₂ (SO ₄)·FeSO ₄ ·6H ₂ O	1.0
Fe(III)	NH ₄ Fe(SO ₄) ₂ ·12H ₂ O	1.0
Hg(II)	HgCl ₂	2.5
Mn(II)	MnSO ₄ ·H ₂ O	5.0
Mo(II)	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	2.5
Mg(II)	MgSO ₄ ·7H ₂ O	5.0
Ni(II)	(NH ₄) ₂ SO ₄ ·NiSO ₄ ·6H ₂ O	10
Pb(II)	(CH ₃ COO) ₂ Pb·2H ₂ O	4.0
Th(IV)	Th(NH ₄) ₄ ·6H ₂ O	0.3
Ti(IV)	K ₂ TiO(C ₂ O ₄) ₂ ·2H ₂ O	None
U(VI)	UO ₂ (CH ₃ COO) ₂ ·H ₂ O	5.0
W(VI)	Na ₂ WO ₄ ·2H ₂ O	0.4
Zn(II)	ZnSO ₄ ·7H ₂ O	5.0
Zr(IV)	ZrO(NO ₃) ₂ ·2H ₂ O	None
Ascorbate	NaC ₆ H ₇ O ₆	5.0
Bromide	KBr	None
Chloride	NaCl	2.5
Citrate	Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	None
EDTA	Na ₂ ·EDTA	None
Fluoride	NaF	5.0
Iodide	KI	2.5
Oxalate	(NH ₄) ₂ C ₂ O ₄ ·H ₂ O	None
Phosphate	NH ₄ H ₂ PO ₄	None
Sulfate	K ₂ SO ₄	5.0
Tartarate	(NH ₄) ₂ C ₄ H ₄ O ₆ ·4H ₂ O	None
Thiocyanate	NH ₄ SCN	2.5
Thiosulfate	Na ₂ S ₂ O ₃ ·5H ₂ O	10.0
Thiourea	H ₂ N·CS·NH ₂	5.0

reagent, 5.0 mL of pH 2.8 buffer and 1.0 mL of 0.3% v/v H₂O₂ solutions, varying amounts of foreign ions are added and finally the solutions are made up to 25 mL with distilled water individually. The absorbances of these solutions are measured at 390 nm. The amount of tolerance limit is noted only when the interfering ion causes ± 2 percent error in the absorbance. The tolerance limits of the ions are given in the (Table 3). A number of metal ions such as Ca(II), Cd(II), Co(I), Hg(II), Mg(II), Mo(VI), Mg(II), Pb(II), U(VI) and Zn(II) do not inter-

fer in the determination of vanadium(V). Ag(I), Al(III) and W(VI) do not interfere in the determination when present in 5-fold molar excess. Th(IV) also does not interfere in the determination when present in 3-fold excess. Cr(III), Cr(VI), Bi(III), Ti(IV) and Zr(IV) interfere seriously. The interference of titanium and zirconium can be masked by using 1.0 mL of 1%. Potassium sulfate solution, Bi(III), Cr(III) and Cr(VI) can be masked by the addition of 1.0 mL of 1% thiourea solution.

Among anions tested, bromide, citrate, EDTA, oxalate, phosphate and tartarate interfere seriously in the determination of vanadium(V).

3.12. Applications of the developed method

The color development with 2,3,4-trihydroxyacetophenone-phenylhydrazine (THAPPH) is an advantage in analyzing various samples, in which vanadium can vary over a wide range. The proposed method has been applied for the determination of vanadium(V) in environmental samples (soil and water), tobacco leaves and alloy samples. The results are in perfect agreement with those obtained by direct atomic-absorption spectrometry.

3.12.1. Determination of vanadium(V) in soil samples

Soil samples were collected in different areas around Tirupathi, Chittoor (dist), Andhra Pradesh, India. These samples were analyzed for vanadium content as mentioned in the recommended procedure. The results are reported in Table 4.

3.12.2. Determination of vanadium(V) in water samples

Different synthetic water samples were prepared with the metal ions which are commonly associated with vanadium(V). These synthetic samples were analyzed for vanadium content as mentioned in the recommended procedure. The results are reported in Table 5.

3.12.3. Determination of vanadium(V) in tobacco leaf samples

The tobacco leaf samples were collected at T.S. Palem (village), Chittoor (dist), Andhra Pradesh (state), India. These samples were analyzed for vanadium content as mentioned in the recommended procedure. The results are reported in Table 6.

3.12.4. Determination of vanadium(V) in alloys samples

Certified standard alloy samples were taken for the determination of vanadium. The results are compared with certified values and also AAS. The results are mentioned in Table 7.

The results obtained in all the above are in good agreement with the results obtained by direct AAS. According to our observations the amount of vanadium in soil samples and

Table 4 Determination of vanadium(V) in soil samples.

Area of sample collected	Vanadium(V) found (µg/g)		Percentage of recovery	SD		RSD (%)		F-test
	AAS method	Present method		AAS method	Present method	AAS method	Present method	
Maruthi Nagar	16.22	16.25	99.81	0.0026	0.0024	0.025	0.023	1.18
Srinivasa Mangapuram	16.02	16.04	99.87	0.0019	0.0020	0.012	0.012	1.00
Karkambadi	17.21	17.30	99.47	0.0016	0.0018	0.014	0.016	1.31
Rangampet	16.86	16.92	99.64	0.0030	0.0032	0.029	0.032	1.14

Table 5 Determination of vanadium(V) in water samples.

S. No.	Composition of synthetic sample ($\mu\text{g/mL}$)	Vanadium found ($\mu\text{g/mL}$)		Percentage of recovery	SD		RSD (%)		F-test
		AAS method	Present method		AAS method	Present method	AAS method	Present method	
Sample 1	V(V) – 8.0, Mo(VI) – 4.0, Ni(II) – 5.0.	7.86	7.85	98.12	0.0032	0.0037	0.031	0.035	1.27
Sample 2	V(V) – 10.0, Ti(IV) – 6.0, Bi(III) – 5.0.	9.64	9.75	97.50	0.0025	0.0024	0.021	0.019	1.22
Sample 3	V(V) – 12.0, Cu(II) – 2.0, Fe(III) – 6.0	11.94	11.96	99.66	0.0036	0.0036	0.015	0.015	1.00

Table 6 Determination of vanadium(V) in *Nicotina tobaccum* (tobacco) leaves.

Vanadium added (μg)	Vanadium found (μg)		Percentage of recovery	SD		RSD (%)		F-test
	AAS method	Present method		AAS method	Present method	AAS method	Present method	
–	18.36	18.16	98.91	0.0038	0.0042	0.027	0.029	1.15
10	28.12	27.95	99.39	0.0038	0.0036	0.026	0.024	1.17
20	38.60	38.16	98.86	0.0024	0.0025	0.019	0.021	1.22

Table 7 Determination of vanadium(V) in alloy samples.

Name of the sample	Composition	Vanadium found (μg)		Percentage of recovery	SD		RSD (%)		F-test
		AAS method	Present method		AAS method	Present method	AAS method	Present method	
BCS-CRM484 (high speed tool)	W, 22.4; Cr, 5.17; V, 0.94; Mo, 1.07; Co, 10.2; C, 0.85; Si, 0.20; S, 0.024; P, 0.30; Mn, 0.21	0.94	0.92	97.87	0.027	0.026	0.045	0.043	1.09
BCS-CRM485	W, 18.2; Cr, 5.15; V, 10.5; Mo, 0.67; Co, 5.06; C, 0.89; Si, 0.22; S, 0.043; P, 0.040; Mn, 0.50	10.5	10.3	98.09	0.021	0.024	0.024	0.027	1.26

tobacco leaves is not exceeding $18.36 \mu\text{g/mL}$ it is observed that when the sample exceeds the threshold limit values (reported is $0.5 \mu\text{g/mL}$ of air and $0.1 \mu\text{g/mL}$ of fume), it showed significant effect on human health and causes diseases like anemia, bronchopneumonia and irritation of mucous membrane. Due to this reason it is very important to determine vanadium in soil samples and tobacco leaves.

4. Conclusion

The present investigations have proved that 2,3,4-trihydroxy acetophenonephenylhydrazone (THAPPH) was a selective and sensitive chelating reagent for kinetic spectrophotometric determination of V(V). The present method was not laborious and there was no need for heating the components. The molar absorptivity ($1.999 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$) value of the complex reveals that the reagent was more sensitive for V(V) than its earlier reagents. A number of associated elements do not interfere with its determinations. The selectivity of the reagent is also improved by judicious use of masking agent to suppress the interference of metal ions like Ti(IV), Zr(IV), Bi(III), Cr(III) and Cr(IV). This method is successfully applied for the determination of V(V) in environmental and alloy samples.

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