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HIGHLY SELECTIVE DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) IN STEELS, MINERALS AND SOIL SAMPLES

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ABSTRACT

A simple, selective and sensitive spectrophotometric method has been developed for the determination of trace amounts of Vanadium(V) in acetic acid medium using a newly synthesised reagent acetoacetanilide salicyloylhydrazone (AASH). The molar absorptivity and Sandell's sensitivity of the coloured species were found to be 1.20 x 10^4 L mol^{-1} cm^{-1} and 4.2 ng cm^{-2} respectively. Beer's law is obeyed in the range 0.3 -3.0 µg mL^{-1} of vanadium(V) at 405 nm. The stoichiometry of the complex was found to be 1:1 (V(V): AASH). A highly selective first order derivative spectrophotometric method for the determination of vanadium is also reported. A calibration graph was derived by measuring first derivative amplitudes at 430 nm (trough depth). The metal ions

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which are normally associated with vanadium in minerals and alloys do not interfere. The developed procedure has been successfully applied for the trace level determination of vanadium in steels, minerals and soil samples.

1. Introduction

The determination of trace amounts of vanadium is of great interest because of the high toxicity of its compounds and its increasing industrial applications [1]. Environmental scientists have declared vanadium as a potentially dangerous chemical pollutant that can play havoc with the productivity of plants, crops and the entire agricultural system. High amounts of vanadium are said to be present in crude petroleum and heavy oil. Power and heat producing plants using fossil fuels cause the discharge of vanadium into the environment [2]. Vanadium has also been reported as the index element in urban environment pollution, especially air pollution. Acute vanadium poisoning is characterized by nervous depression, coughing, vomiting, diarrhoea, negative effects on lever and kidney and increased risk of lung cancer [3]. Hence the accurate determination of vanadium at trace levels using simple and rapid methods is of great importance. Various analytical techniques used for the determination of vanadium in environmental samples include NAA [4], ICP-AES [5] and AAS [6] and spectrophotometry. Spectrophotometric methods occupy special position due to their simplicity, less expensive instrumentation and high sensitivity. Kinetic spectrophotometric methods based on the catalytic action of vanadium(V) on the oxidation of organic compounds with inorganic reactant (eg. bromate or periodate) are highly sensitive but are generally lacking simplicity or a long time is necessary to complete the reaction [7-10]. The most widely used reagent for vanadium(V) determination is pyridyl azo resorcinol (PAR), but many of these methods suffers from limitations such as serious interference from U(VI), Ti(IV), Zr(IV), and Nb(V) ions, the delay in colour development and also significant absorbance for the reagent blank solution [11-13]. Other reagents have been suggested for the spectrophotometric determination of vanadium include 1, 10-phenanthroline [14], ferron [15], 2-(2-quinolylazo)-5-diethylaminophenol [16], methdilazine hydrochloride [17], picolinealdehyde salicyloylhydrazone [18], 2,4-dihydrxyacetophenone benzoylhydrazone and pyridine [19] and pyrogallol [20]. Most of these methods suffer from limitations such as tedious and time consuming extraction [15,18], low selectivity [16], reduction to lower oxidation state followed by extraction [19] or lack of sensitivity [14,17].

In the present investigation we report a simple, selective and non-extractive derivative spectrophotometric determination of vanadium(V) using a newly synthesized reagent acetoacetanilide salicyloylhydrazone (AASH) in acetic acid medium. The derivatisation of the spectral profiles enhances the selectivity of the method as closely overlapped absorption bands of the interfering ions become resolved [21]. The distinct advantage of the proposed method is that the commonly associated metal ions especially Fe, Mo, Mn, Co, Cr and Ni could be tolerated in considerable excess. The method has been successfully applied for the determination of vanadium in steels, minerals and soil samples.

2. Experimental

Apparatus

A Shimadzu 1601 UV/VIS. Spectrophotometer equipped with 1.0 cm quartz cells was used for all spectral measurements. The instrumental parameters were optimised and the best results were obtained with a scan speed 370 nm/min., slit width of 1 nm and $\Delta\lambda$ =2 nm for the first order derivative mode in the wavelength range 350 – 650 nm. A Systronics µ pH system 362 was used for pH measurements.

Reagents

All chemicals used were of analytical grade. A stock solution of vanadium(V) (1000 $\mu g mL^{-1}$) was prepared by dissolving an accurately weighed amount of sodium metavanadate (s. d. fine-chem. Ltd. India) in distilled water and made up to the mark in a 100 mL volumetric flask. This stock solution was standardised [22] and working solutions were prepared by diluting the stock solution to an appropriate volume. Solutions of the studied interfering ions of suitable concentrations were prepared using A.R. grade reagents. A 0.1% solution of AASH was prepared in ethanol. A 10 M acetic acid solution was used throughout the study.

Synthesis of AASH

Acetoacetanilide salicyloylhydrazone was synthesised by refluxing equimolar amounts of acetoacetanilide and salicyloylhydrazide in ethanolic medium for 2 hours. The resulting hydrazone was recrystalised from ethanol (m.p. =196 °C, yield, 75 %). IR spectra of AASH (KBr) showed bands at 3271 cm^{-1} (ν_{NH}), 3413 cm^{-1} (ν_{OH}), 1647 cm^{-1} ($\nu_{C=O}$), and 1543 cm^{-1} ($\nu_{C=N}$). The signals in ^1H NMR (DMSO-d_6) spectrum of AASH are assigned as follows. The -OH proton appeared as a singlet at δ, 11.07 integrating for one proton. The two -NH proton signals appeared in the region δ, 10.21-10.33. The aromatic protons resonated at δ, 6.97-7.92 as multiplets (Figure 1).

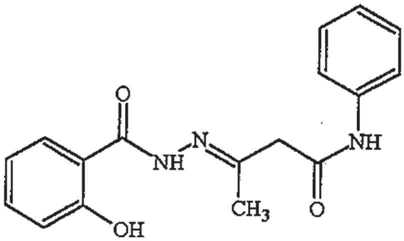

Fig 1 : Structure of AASH

General procedure

Aliquots of the solution containing 3.0-30.0 μg of vanadium(V) were transferred into a series of 10.0 mL calibrated volumetric flasks. To these were added AASH (0.1%, 2 mL) and acetic acid (10 M, 4 mL) and the contents were diluted to the mark with distilled water and mixed well. The absorbance of the coloured species was measured at 405 nm against the corresponding reagent blank.

The first order derivative spectra were recorded with reference to the reagent blank in the wavelength range 350-600 nm. The concentration range applicable to derivative mode was 0.2-3.5 μg ml^{-1} of vanadium(V). In the derivative spectrum trough depth (TD) at 430 nm was measured from the zero line of the spectrum to determine its dependence on the metal ion concentration. Calibration graph was constructed by plotting the derivative amplitudes against the concentration of vanadium(V) ions.

Analysis of vanadium steel

An accurately weighed amount of alloy steel sample (0.5 g.) was dissolved completely in 10 mL of aqua regia by slow heating on a sand bath and then heated to fumes of oxides of nitrogen. After it was cooled, sulphuric acid (5 mL, 1:1) was added and evaporated almost to dryness. The residue left over was treated with 20 mL of distilled water and filtered. The filtrate was diluted to 50 mL with distilled water. Potassium permanganate solution (0.002 M) was added drop wise till the solution attained pink colour. It was allowed to stand for 5 min, and then warmed and oxalic acid solution (0.0025 M) was added slowly with constant stirring till the disappearance of pink colour. The solution was diluted to 100 mL with distilled water. Citrate solution was used to mask iron wherever necessary. Suitable aliquots of sample solutions were analysed for vanadium according to the procedure for first derivative spectrophotometry.

Analysis of vanadium in ilmenite mineral samples

Finely powdered ilmenite (about 0.5 g.) was weighed accurately into a silica crucible and fused with sodium hydrogen sulphate (10 g.) until the sample was completely decomposed. The melt was cooled and dissolved in (2 M, 25 mL) sulphuric acid, filtered. The filtrate was treated with potassium permanganate and oxalic acid solution as described for the analysis of vanadium steels and diluted to 100 mL with distilled. Citrate solution was used to mask iron wherever necessary.Suitable aliquots of sample solutions were analysed according to the procedure for first derivative spectrophotometry.

Determination of vanadium in soil samples

A known amount of (1 g.) air dried homogenized soil samples, spiked with known amounts of vanadium(V) was taken and brought into solution by following the standard method recommended by Jackson [23]. A suitable aliquot of the solution was taken and analysed using the procedure outlined earlier.

3. Results and Discussion

Preliminary investigations have shown that AASH reacts with vanadium(V) in acetic acid medium at room temperature to form an yellow coloured species, which shows maximum absorbance at 405 nm. The reagent blank had negligible absorbance at this wavelength. The absorption spectra of the coloured species against reagent blank under the optimum conditions are presented in Figure 2.

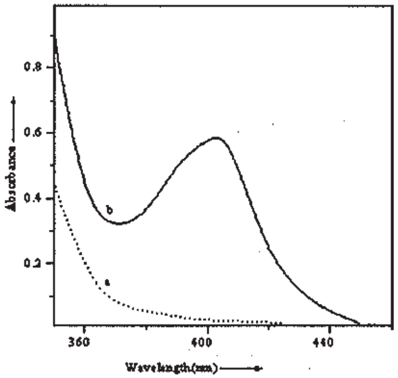

Fig 2 : Absorption (zero order) spectra of (a) reagent blank vs distilled water and (b) V(V)-AASH complex (Vanadium, 2.4 µg mL^{-1}) vs reagent blank., each containing 2 mL of 0.1% AASH and 4 mL of 10 M acetic acid in a total volume of 10 mL.

Effect of acidity

The effect of different acids on the absorbance of vanadium(V)-AASH species has been investigated using H_3PO_4, HCl, HNO_3, H_2SO_4 and CH_3COOH. It was observed that colour formation of the complex was slow in phosphoric acid medium. The colour intensity was less in nitric acid, hydrochloric acid and sulphuric acid media. CH_3COOH medium (3 M-6 M) was found to be optimum for this analytical work because of higher sensitivity and longer stability of the coloured species (figure 3). Hence 4 mL of 10 M CH_3COOH in a total volume of 10 mL was preferred for further analytical studies.

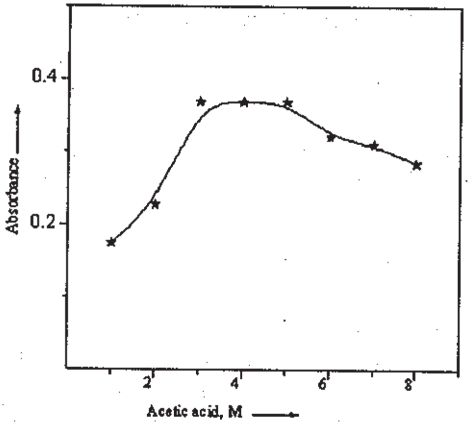

Fig 3 : Effect of acetic acid concentration on the absorbance of V(V)-AASH species (vanadium, 1.6 μg mL^{-1})

Effect of reagent concentration

Different molar excess of AASH were added to fixed metal ion concentration and absorbance were measured according to the standard procedure. A 10- fold molar excess of AASH is found to be necessary for maximum and constant colour development for 1 μg mL^{-1} of vanadium(V). Excess of reagent had no effect on the sensitivity and stability of the complex. For up to 35 μg of vanadium(V), the addition of 2 mL of 0.1 % AASH was found to be sufficient to complete the reaction. Under the optimum conditions the absorbance of the complex was found to remain constant at least for 6 hours at room temperature, which showed that these coloured species are stable.

Analytical parameters

The molar absorptivity and Sandell's sensitivity values of V(V)-AASH species calculated from Beer's law data are 1.20×10^4 L mol^{-1} cm^{-1} and 4.2 ng cm^{-2} respectively. Beer's law is obeyed in the range of 0.3-3.0 μg mL^{-1}. The linear regression analysis of absorbance, [A] at λ_{max} of the complex versus metal ion concentrations (μg mL^{-1}), shows a good linear fit (Table 1).

Table 1: Analytical characteristics of V(V)-AASH complex

Parameters	**Normal 405 nm**	**First derivative 430 nm**
Molar absorptivity (L mol^{-1} cm^{-1})	1.20×10^4	-
Sandell's sensitivity (ng cm^{-2})	4.2	-
Detection limit C_L (k=3) (μgmL^{-1})	7.6×10^{-2}	2.8×10^{-2}
Quantitation limit C_Q (k=10) (μgmL^{-1})	2.5×10^{-1}	9.5×10^{-2}
Regression equation (y)[a]		
Slope, m	0.2354	0.0104
Intercept, c	-0.008	-0.0004
Correlation coefficient, r	0.9996	0.9998
RSD %	1.14	0.92

[a] $y = mx + c$ where y, absorbance/peak height/ trough depth; m, slope; x, analyte concentration (μgmL^{-1}); c, intercept.

First order derivative spectra of V(V)-AASH complex shows a small peak at 395 nm, a trough at 430 nm and a cross over point at 405 nm, corresponding to the λ_{max} of the complex (Figure 4). The derivative amplitudes measured at 430 nm were found to be proportional to the concentration of vanadium(V). The characteristics of calibration graph are given in Table 1. The high value of correlation coefficient and closeness of the intercept to zero show that calibration graphs are linear and obey Beer's law. The derivative method allowed the determination of vanadium(V) in the range 0.2-3.5 μg ml^{-1} at 430 nm.

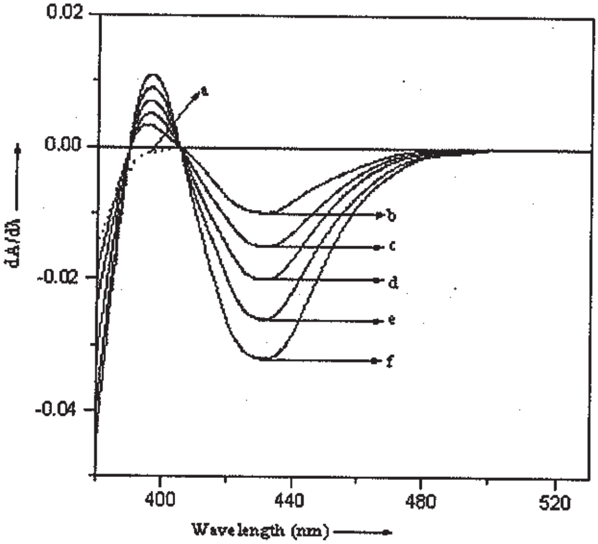

Fig 4 : First order derivative spectra of V(V)-AASH system: (a) Reagent blank vs distilled water, (b-f) contain increasing amounts of V(V) up to 3.5 μgmL^{-1} and all other conditions are as described in figure 2.

Limit of detection C_L (k=3) and limit of quantification C_Q (k=10) in normal and derivative modes as defined by IUPAC, are reported in Table 1. The precision of the method in different modes, reported as relative standard deviations, RSD determined by measuring absorbance or derivative amplitude of five replicate samples containing 1.5 μg mL^{-1} of vanadium(V).

Stoichiometry and stability constant

The stoichiometry of the complex was investigated by Job's continuous variation method and mole ratio method and was found to be 1:1 (V(V):AASH). The stability constant of complex was determined by limiting logarithmic method [24] and was found to be 2.86×10^7. The nature of the species was investigated by passing an aliquot of the solution through a cation (Amberlite IR 120) and an anion (Amberlite IRA 400) exchange resin. Only cation exchange resin retained the coloured species, indicating the cationic nature of the species.

Isolation of the coloured species was done by extraction into chloroform phase. The reagent was found to be not soluble in the solvent. The extract on slow evaporation yielded a solid product. Characterisation of isolated species was done by IR and NMR spectral analysis. The –OH and –NH proton signals in the ^1H NMR spectra of both the complexes remained more or less in the same positions as in the free ligands indicate that neither groups are deprotonated or involved in coordination. In the IR spectrum, appearance of ν_{OH} and ν_{NH} bands in the same position as in the free ligands suggesting non-involvement of these groups in bonding. The band due to $\nu_{C=N}$ and $\nu_{C=O}$ merged and appeared at 1600 cm^{-1} indicating involvement of these groups in coordination. Band due to VO_2 is observed at 970-975 cm^{-1}. Broad band appeared around 3400-3500 cm^{-1} indicates coordinated water molecules. The most probable structural formula of the chelate is proposed in figure 5.

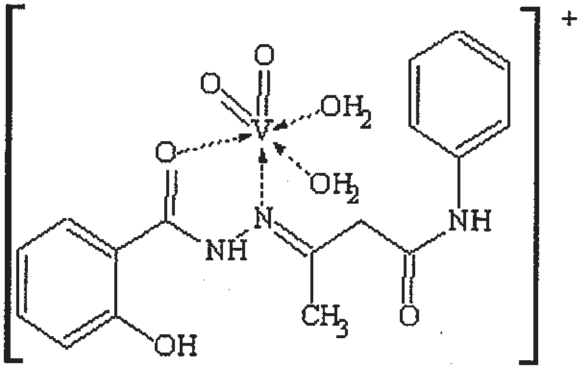

Fig 5 : The probable structural formula of V(V)-AASH species.

Effect of diverse ions

To assess the usefulness of the proposed method the effect of diverse ions on the trace level determination of vanadium (1.5 µg mL^{-1}) has been investigated in normal and in first derivative modes. The tolerance limit was taken to be the amount that caused a ±3% change in absorbance. The tolerance limits of the foreign ions tested are given in Table 2. Alkali and alkaline earth metal ions and a large number of anions did not interfere even when present in large excess. Cations like Co(II), Ni(II), Mn(II), Mo(VI), and Cr(III) which are usually associated with vanadium containing samples did not interfere in both zero order and derivative modes. The most serious interference was from Zr(IV) ions due to the complex formation with AASH. The measurement in the first derivative mode at 430 nm (zero-crossing point of Zr(IV)-AASH complex) increases the tolerance limit of Zr(IV) up to 20-fold excess. Thus the selectivity of the method is considerably enhanced by recording spectra in the derivative mode without any pre-separation or addition of masking agents.

Table 2 : Tolerance limit of diverse ions in the determination of 1.5 μg mL^{-1} Vanadium(V)

Ions	Tolerence limit (μg mL^{-1})	Ions	Tolerence limit (μg mL^{-1})
Co(II)	800	Zr(IV)	5(30)[b]
Mn(II)	700	Al(III)	800
Ni(II)	750	Mo(VI)	500
Cr(III)	300	Cu(II)	500
Na(I)	3000	Ti(IV)	600
K(I)	3000	Chloride	5500
Ca(II)	2000	iodide	2000
Sr(II)	1500	bromide	3000
Ba(II)	2500	nitrate	5000
Mg(II)	1500	phosphate	2500
Pb(II)	500	sulphate	3500
Zn(II)	500	fluoride	3000
Hg(II)	400	oxalate	1000
Fe(III)	70(1000)[a]	EDTA	400

[a] In the presence of 3 mg mL^{-1} of citrate; [b] Measurement in the derivative mode

Analytical applications

The proposed method was applied to the quantitative determination of vanadium(V) in steel and ilmenite samples. Based on the better sensitivity and selectivity measurement of derivative amplitudes at 430 nm is recommended for the determination of vanadium in various samples. The results of the analysis presented in Table 3 are in good agreement with the certified values. The low relative standard deviation values for analysis of five replicates indicated good precision of the proposed methods.

Table 3 : Determination of vanadium(V) in vanadium steels and ilmenite

Sample	Composition %	Vanadium %		RSD %
		Certified	found [a]	
Vanadium steel 7110 b	C, 0.18; Si, 0.34, Mn, 0.33; Ni, 0.12; Cr, 1.08; Mo, 0.85; V, 0.87; Cu, 0.22; P, 0.018; S, 0.012; Ti, 0.11; Al,0.042; B, 0.0009.	0.87	0.865	0.87
Vanadium steel T032 b	C, 0.56; Si, 0.24; Mn, 0.91; Ni,0.23; Cr, 1.03; Mo, 0.03; V, 0.12;Cu, 0.19; P, 0.002; S, 0.018.	0.12	0.121	1.00
Diesteel H13 Grade EA 0958	C, 0.370; Si, 0.974; Mn, 0.364; P, 0.024; S, 0.006; Cr, 4.962; Ni, 0.318; Mo, 1.254; V, 0.994.	0.994	0.99	0.85
Ilmenite Q Grade	TiO_2, 60.6; Fe_2O_3, 24.2; FeO, 9.3; Al_2O_3, 0.96; MnO, 0.39; Cr_2O_3, 0.12; MgO, 0.89; P_2O_5, 0.21; V_2O_5, 0.15; ZrO_2, 0.90; SiO_2, 0.41; Rare earths, traces 2.0.	0.15	0.151	1.15
Ilmenite MKGrade	TiO_2, 54.2; Fe_2O_3, 14.2; FeO, 26.6; Al_2O_3, 1.25; MnO, 0.4; Cr_2O_3, 0.07; MgO, 1.03; P_2O_5, 0.12; V_2O_5, 0.16; ZrO_2, 0.80; SiO_2,0.68; Rare earths, traces 0.34.	0.16	0.162	1.08

[a] Mean value of five determinations.

Statistical analysis of the results in comparison with the standard method.

The results of the analysis of soil samples were compared statistically by the students t-test and by the variance ratio F-test with those obtained by the reported method [25]. The students t-values and the variance ratio F-values did not exceed the theoretical values, indicating that there was no significant difference in accuracy and precision between proposed and reference method. The results are given in Table 4.

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

Sample	V(V) added mg mL^{-1}	Proposed method^a mg mL^{-1}	RSD %	Reference method^a mg mL^{-1}	RSD %	Comparison with the reference method	
						F-test ^{b}	t-test ^{c}
Soil 1	1.60	1.61	1.36	1.59	1.17	1.34	1.52
Soil 2	2.40	2.41	0.82	2.42	0.78	1.10	1.11

[a] Mean value of five determinations.
[b] Tabulated F-value for (4,4) degree of freedom at p (0.95) is 6.39.
[c] Tabulated t-value for (4,4) degree of freedom at p (0.95) is 2.78.

4. Conclusion

The proposed method offers the advantages of high sensitivity, selectivity and simplicity for the determination of vanadium(V) without the need for organic solvent extraction, pre-concentration or pre-separation. The proposed method can be used as an alternative method for the determination of trace amounts of vanadium in mineral, alloys, urine and soil samples as the associated metal ions in these materials do not interfere with the determination.

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