

Direct and derivative Spectrophotometric determination of Vanadium (V) using 3-methoxysalicylaldehyde isonicotinoylhydrazone reagent

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ABSTRACT

Vanadium (V) forms a yellow coloured water soluble complex with 3-methoxysalicylaldehyde isonicotinoylhydrazone (MSIH) reagent in acidic buffer pH 4.75 with λ_{max} at 346 nm. The Molar absorptivity and Sandell's sensitivity are $8.1 \times 10^4 \text{ L Mole}^{-1} \text{ cm}^{-1}$ and $0.00629 \mu\text{g} / \text{cm}^2$ respectively. The Beer's law validity range is 0.051 to $0.51 \mu\text{g} / \text{mL}$. Vanadium (V) forms (M: L) 1:2 complex with MSIH and stability constant of the complex is 7.7×10^{15} . The developed Second derivative Spectrophotometric method was employed for the determination of Vanadium (V) in alloy samples. The effect of various diverse ions also studied.

Key-words: 3-Methoxysalicylaldehyde isonicotinoylhydrazone (MSIH), Spectrophotometry, Vanadium (V) determination.

The chemistry of vanadium is very complex. It has good resistance to corrosion by alkali metals, sulfuric acid and hydrochloric acid. Common oxidation states of Vanadium include +2, +3, +4 and +5. Approximately 80 % of Vanadium produced is used in ferrovanadium or as a steel additive. Vanadium finds numerous applications because of its properties such as strength and rust resistance to alloys. Vanadium pentoxide is used as a catalyst in manufacturing of sulfuric acid (via contact process) and maleic anhydride. It is also used in making ceramics. Vanadium is an essential component of some enzymes, particularly the vanadium nitrogenase is used by some nitrogen-fixing micro-organisms. Vanadium compounds are poorly absorbed through the gastrointestinal system and hazardous to mammals. Inhalation exposures to vanadium and vanadium compounds result primarily in adverse effects to the respiratory system.

Hydrazones are important organic analytical reagents for the determination of metal ions in microgram quantities. They react with many metal ions forming coloured complexes and act as chelating agents. In general, the technique of solvent extraction is widely used in the spectrophotometric determination of metal ions. However organic solvents

such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction. The potential application of hydrazone derivatives for the Spectrophotometric determination of metal ions has been reviewed by Singh et al.¹. In the light of good analytical characteristics of hydrazones, herein we report direct and second order derivative Spectrophotometric determination of V (V) in aqueous medium using MSIH without involving any extraction.

Derivative Spectrophotometry is a very useful technique, in the sense that, it decreases the interference i.e. increases the tolerance limit value of the foreign ions. The great interest towards derivative spectrophotometry is due to the increased resolution of spectral bands, allowing the detection and location of the wavelengths of poorly resolved components of complex spectra and reducing the effect of spectral background interferences. Because of these characteristics, the process of isolation and pre-concentration of active components, usually required in qualitative and quantitative spectrophotometric procedures applied in the analysis of complex systems, is completely avoided. Derivative Spectrophotometric methods for the determination of metal ions²⁻⁴ are not exploited much.

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Materials and Methods

Apparatus;

Spectrophotometric measurements were made on a Shimadzu 160A microcomputer based UV-Visible spectrophotometer equipped with 1.0 cm quartz cells. An ELICO LI-120 digital pH meter was used for pH adjustments.

Reagents;

All reagents used were of A.R grade unless otherwise stated. All solutions were prepared with distilled water.

Synthesis of 3-methoxysalicylaldehyde isonicotinoylhydrazone (MSIH) reagent;

The reagent 3-methoxysalicylaldehyde isonicotinoylhydrazone (MSIH) was prepared by simple condensation of 3-methoxysalicylaldehyde with Isonicotinoylhydrazide. In a 250 mL round bottom flask, hot methanolic solution of 3-methoxysalicylaldehyde (1.5g, 0.01 mole) and Isonicotinoylhydrazide (1.37 g, 0.01 mole) are mixed and refluxed by using water condenser for 3 h. On cooling the reaction mixture, a greenish yellow coloured product was separated out, collected by filtration, washed with cold methanol, yield 60%, M.P 228°C.

The mass spectrum of MSIH shows a molecular ion (M) peak at 271.1(m/z) corresponding to its molecular weight and (M+I) peak at 271.9. The Infra red spectrum of MSIH shows bands at 1690.7(s), 3200.99(b), 3003.17(m), 1566.85(s) cm^{-1} for $-\text{C}=\text{O}\% \text{NH}$, Intermolecular $-\text{O}-\text{H}$, $-\text{C}-\text{H}$ stretch, imine group ($=\text{N}-$) respectively. ^1H NMR spectrum recorded in DMSO shows the delta value 12.2 (s, 1H, NH), 10.7 (s, 1H, OH), 8.8 (s, 2H, Pyridyl), 8.7 (s, 1H, C=N-H), 7.7 (m, 2H, Pyridyl), 7.4 (d, 1H, ArH), 7.1 (d, 1H, ArH), 6.9 (m, 1H, ArH), 3.8 (s, 3H, CH_3) and the structure is confirmed based upon NMR, IR and Mass spectral data given in Figure 1.

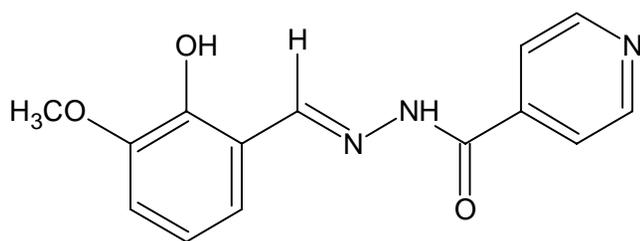


Fig.1: Structure of 3-methoxysalicylaldehyde isonicotinoylhydrazone (MSIH)

The reagent solution (0.01 M) was prepared by dissolving 0.271g of 3-Methoxysalicylaldehyde isonicotinoylhydrazone (MSIH) in 100 mL of Dimethylformamide.

The standard Vanadium (V) solution (0.01M) was prepared by dissolving 0.117 g of Ammonium metaVanadate

(A.R LOBA) in minimum amount of hot distilled water and diluted up to the mark in a 100-mL standard flask.

Buffer solutions were prepared by 1M Hydrochloric acid – 1M Sodium acetate (pH 0.5-3.5); 0.2 M Acetic acid - 0.2 M Sodium acetate (pH 4.5-7.0); 2M Ammonium chloride - 2M Ammonium hydroxide (pH 7.5-12.0).

Reaction with metal ions;

The reactions of some important metal ions were tested at different pH solutions. The samples were prepared in 10-mL volumetric flasks by adding 4 mL of buffer (pH, 1.0- 11.0), Metal ion (0.5 mL of $1 \times 10^{-3}\text{M}$), and MSIH (0.5 mL of $1 \times 10^{-2}\text{M}$) solution. The mixture was diluted up to the mark with distilled water. The absorbance was measured in 350- 600 nm range against reagent blank. The results are summarized in Table- 1.

Table - 1:
Analytical Characteristics of 3-methoxysalicylaldehyde Isonicotinoylhydrazone (MSIH)

Metal ion	pH	λ_{max} nm	Molar absorptivity ($\text{L Mole}^{-1} \text{cm}^{-1}$) 1×10^4
Co (II)	5.5	435	2.02
Ni (II)	6.0	372	1.02
Al (III)	6.5	394	3.2
V (v)	4.75	346	8.1
U (VI)	4.0	374	1.05

Recommended Procedure;

(i) Determination of V (V) (Zero order Spectrophotometry):

An aliquot of the solution containing 0.051 to 0.51 μg / mL of V (V), 4 mL of buffer solution pH 4.75 and 0.5 mL of $1 \times 10^{-3}\text{M}$ MSIH reagent were taken in a 10- mL volumetric flask and the solution was diluted up to the mark with distilled water. The absorbance of the solution was recorded at 346 nm in a 1.0 cm cell against reagent blank. The measured absorbance was used to compute the amount of Vanadium (V) from the calibration plot.

(ii) Determination of V (V) by Second order derivative Spectrophotometry:

For the above solution of V (V) - MSIH Second order derivative spectrum was recorded with a scan speed having degrees of freedom 9 in a wavelength range 350 nm to 600 nm. The derivative spectrum was measured at peak depth (valley) by measuring the peak zero method at 418 nm. The peak depth (Valley) at 418 nm is proportional to the concentration of Vanadium (V). Therefore, the peak depths were measured at this wavelength for the construction of calibration plots.

Results and Discussion

3-methoxysalicylaldehyde isonicotinoylhydrazone (MSIH) reagent is easily obtained as any other Schiff base reagent. So far the new Chromogenic reagent MSIH was not used for the Spectrophotometric determination of V (V).

The colour reactions of some important metal ions with MSIH are summarized in Table-1. The colour reaction are mainly due to the complex formation of MSIH with divalent, trivalent, pentavalent and hexavalent metal ions such as Ni (II), Co (II), Al (III), V (V), and U (VI) in acidic buffer medium to give intense coloured complexes. In acidic medium, the ligand presumably co-ordinates the metal ions as di-anion to give a neutral complexes.

Vanadium (V) reacts with MSIH in acidic medium to give yellow coloured water-soluble complex. The colour reactions between V (V) and MSIH are instantaneous even at room temperature in the pH range 2.0 – 6.0. The absorbance of the yellow coloured complex remains constant for more than 1 h. The maximum colour intensity was observed at pH 4.75.

A 5-fold molar excess of reagent is adequate for full colour development. The order of addition of metal ion, reagent and buffer solution has no adverse effect on the absorbance of the complex. The complex formation reaction between V (V) and MSIH has been studied in detail based on the composition of the complex as determined by using Job's and molar ratio methods. Important physico-chemical and analytical characteristics of V (V) and MSIH are summarized in Table-2.

The recommended second order derivative procedure has been employed for the determination of V (V). The zero order and Second order derivative spectra of V (V) complex of MSIH are given in Figure 2 and 3 respectively.

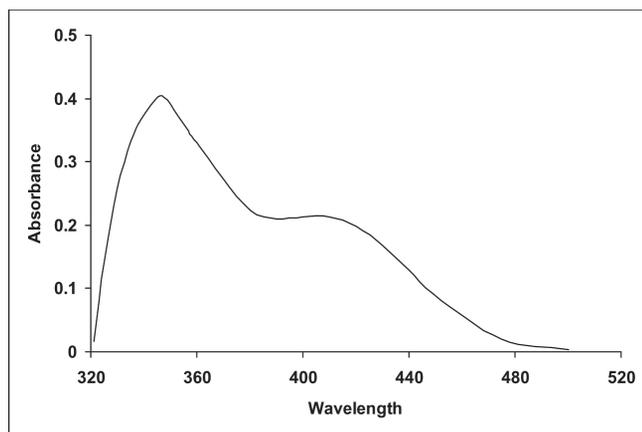


Fig. 2: Zero order Absorption spectra
V (V)-MSIH Complex Vs Reagent blank,
pH 4.75, V (V) 5×10^{-5} M, MSIH 5×10^{-4} M.

Table -2:
Physico-chemical And Analytical Charecteristics of V (V) - Msih Complex

Characteristics	Results
λ_{Max} (nm)	346
pH range (optimum)	.0 – 5.5
Mole of reagent required per mole of metal ion for full colour development	5 folds
Molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)	8.1×10^4
Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$)	0.00628
Beer's law validity range ($\mu\text{g}/\text{mL}$)	0.051 to 0.51
Optimum Concentration range ($\mu\text{g}/\text{mL}$)	0.102 to 0.4588
Composition of complex (M: L) obtained in jobs and mole ratio method	1:2
Stability constant of the complex	7.7×10^{15}
Standard deviation in the determination of $0.25 \mu\text{g}/\text{mL}$ of V (V) for ten determinations	0.009
Relative standard deviation (%)	2.28
Regression Coefficient	0.99

Effect of diverse ions;

The effect of various diverse ions in the determination of V (V) was studied to find out the tolerance limit of foreign ions in the present derivative method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of $\pm 2\%$ in the absorbance or amplitude. The results obtained in derivative method are given in Table-3. The data suggest that several associated anions and cations such as Tartarate, Iodide, Citrate, Tetraborate, Thiosulphate, Sulphate, Phosphate, Lead (II), Silver (I), Tin (II), Uranium (VI), Cobalt (II), Cadmium (II) and Molybdenum (VI) do not interfere when they are

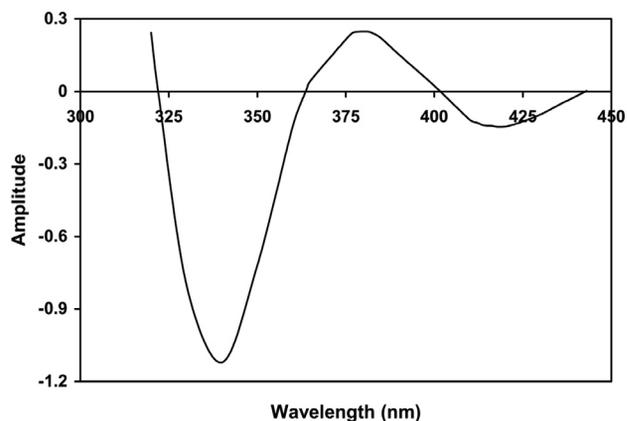


Fig. 3: Second order derivative spectrum of V (V)-MSIH complex.
pH 4.75, V (V) 5×10^{-5} M, MSIH 5×10^{-4} M.

Table - 3:

Tolerance Limit of Foreign Ions in the Determination of 2.22 Mg/MI Vanadium (V) in Second order Derivative Spectrophotometric Method

Ion added	Tolerance limit	Ion added ($\mu\text{g/mL}$)	Tolerance limit ($\mu\text{g/mL}$)
Tartarate	2225	Pb ⁺²	116
Iodide	1904	Ag ⁺	129
Citrate	1894	Sn ⁺²	122
Tetraborate	1842	U ⁺⁶	119
Thio	1682	Co ⁺²	118
Sulphate	1441	Cd ⁺²	112
Sulphate	1424	Mo ⁺⁶	96
Phosphate	1199	Cu ^{+2*}	95
Bromide	880	Mn ⁺²	82
Oxalate	709	Zn ⁺²	65
Chloride	603	Ti ⁺⁴	61
Urea	590	Ca ⁺²	60
Acetate	580	Mg ⁺²	49
ThioCyanide	496	Fe ^{+3 †}	45
Nitrate	379	Bi ⁺³	42
Fluoride	114	Ni ⁺²	29
Thiourea	88	Cr ⁺⁶	26
Ascorbic Acid		Hg ⁺²	20
		W ⁺⁶	15
		Al ⁺³	13
		Ce ⁺⁴	7.0
		Pd ⁺²	1.0

*Masked by thiourea 98 $\mu\text{g/mL}$,

†Masked by Phosphate 1242 $\mu\text{g/mL}$

present in large excess. The tolerance limit values for many anions and cations are more in derivative method. The interference of associated metal ions such as Iron (III) and Copper (II) were decreased with masking agents phosphate and thiourea respectively.

Applications;

The proposed method was successfully applied for determination of Vanadium (V) in alloy samples. 0.5g of sample was heated in 20 mL of aquaregia for digestion, 3 mL of 15% H₂O₂ was added drop by drop. The solution was heated and evaporated to nearly dryness. The residue was dissolved in a 50 mL of distilled water, filtered and made up to the mark in a 100-mL flask. V (V) in this solution was determined by the recommended derivative procedure from a predetermined calibration plot and results presented in Table-4

Table - 4:

Estimation Of Vanadium (V) In Alloy Samples

Sample	Amount of Vanadium(V)%		Error (%)
	Certified	Found*	
Ferro-Vanadium BCS-205/3 ^a	50.16	48.96	2.4
Ilmenite ^b	0.12	0.114	5.0

*Average of best three determinations among five determinations

^a 0.053 % Ni (II), 0.414% Al (III), 0.054 % Cu (II), 47.21 % Fe (III), 50.16 % V (V)

^b 60.6 % Ti (VI), 14.2 % Fe (III), 26.6 % Fe (II), 1.25 % Al(III), 0.4 % Mn (II), 0.07 % Cr

(III), 1.03% Mg (II), 0.08 % Zr (IV), 0.16 % V (V), 0.12 % rare earths

Conclusions

The present method using 3-methoxysalicylaldehyde isonicotinoylhydrazone (MSIH) as Spectrophotometric reagent for the determination of Vanadium (V) in aqueous medium is sensitive and simple. This method was favorably compared with previously reported Spectrophotometric methods⁵⁻¹¹ presented in Table-5. Most of the Spectrophotometric methods involve either extraction^{6,7} or heating of the reaction mixture. However heating at a specific temperature for a long time or extraction of components is laborious and time consuming. The determination of Vanadium (V) using MSIH is not laborious and there is no need of heating the components or extraction. Further, the reagent is easy to synthesize using available chemicals. Moreover, the present method is simple, rapid, reasonably sensitive and selective for the determination of Vanadium (V).

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Table – 5:

Comparison of Spectrophotometric Methods for the Determination of V (V)

Reagent	λ_{\max} (nm)	pH	Molar absorptivity (ϵ) ($L \text{ mol}^{-1} \text{ cm}^{-1}$)	Extraction/heating	Beers law range	Ref
2,5-dihydroxy acetophenone benzoylhydrazone	410	-	1.05×10^4	-	0.25 – 6.0	5
2,4-dihydroxy acetophenone benzoylhydrazone	363	AcOH medium	2.83×10^4	Extn Benzene	0-1.5 mg/mL	6
2'-hydroxy acetophenone benzoylhydrazone	375	AcOH medium	8.93×10^3	Extn CHCl_3	0-3.5 mg/mL	7
Variamine blue	570	-	1.65×10^4	-	0.1-2.0 $\mu\text{g/mL}$	8
5,7-dibromo-8-hydroxyquinoline	400	Acidic medium	6.1×10^3	-	0.1-20 $\mu\text{g/mL}$	9
Salicylideneamino-4-hydroxybenzene sulfonic acid	420	4.0-6.5	1.14×10^4	-	0-100 $\mu\text{g/25mL}$	10
2,5-di (2-phenol)-1,3,4-thiadiazole	480	4.6	6.8×10^4	-	0.1-2.4 mg/mL	11
3-methoxy salcinaldehyde isonicotinoylhydrazone	346	4.75	8.1×10^4	-	0.051-0.51 $\mu\text{g/mL}$	Present method

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