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Synthesis, Characterization and Spectrophotometric Determination of Vanadium(V) with Unsubstituted Cinnamoyl Hydroxamic Acid

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A series of hydroxamic acid and their derivatives play a key role in chemistry and metallochemistry in the subject of study of many synthetic experimental investigations. In this paper the synthesized compound were characterized and their structure was confirmed by standard spectroscopic method ^{1}H NMR and IR spectrum. The determination of vanadium(V) in water and soil samples has been determined by spectrophotometric method using cinnamoyl hydroxamic acid as reagent.

Keywords: Vanadium(V), Hydroxamic acid, Spectrophotometric method.

INTRODUCTION

Hydroxamic acids are compound, RC(=O)NHOH, derived from oxoacids by replacing –OH by –NHOH and hydrocarbyl derivatives there are specific examples preferably named as N-hydroxyl amides [1]. They contain the carbonyl group (CO) and a hydroxylamine as NH_2OH and have following structure (Fig. 1).

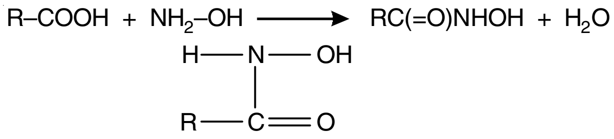


Fig. 1. General structure of hydroxamic acid, where R as an alkyl and aryl group

Literature reported the synthesis of many hydroxamic acid and their derivatives [2-8]. In this paper deals the synthesis of unsubstituted cinnamoyl hydroxamic acid, is derived from acylation of acid chloride or acid anhydrides. Hydroxamic acid and their derivatives have been recognized as metal chelators [9], pathological compound and useful in drug [10-14] development process. In this paper spectrophotometric method is based on the purple coloured complex reaction between organic reagents unsubstituted cinnamoyl hydroxamic acids and vanadium(V) metal ion [15-18] thus form stable 5 membered inner chelates compounds. It is deprotonation process and act as either hydroxamato- or hydroxamato-2 ligands, which behave as monodentate as well as bidentate ligands [19]. Organic reagent cinnamoyl hydroxamic acid containing as oxygen donor ligand most easily forms complex with vanadium(V) metal ions [20-22] shown in below (Fig. 2).

EXPERIMENTAL

Cinnamoyl hydroxylamine was procured from Sigma Aldrich. All the chemicals used during the experimental work were obtained from Merck and of AR grade. Melting points were determined on a melting point apparatus and also determined by Thiele's tube using liquid paraffin by open capillary

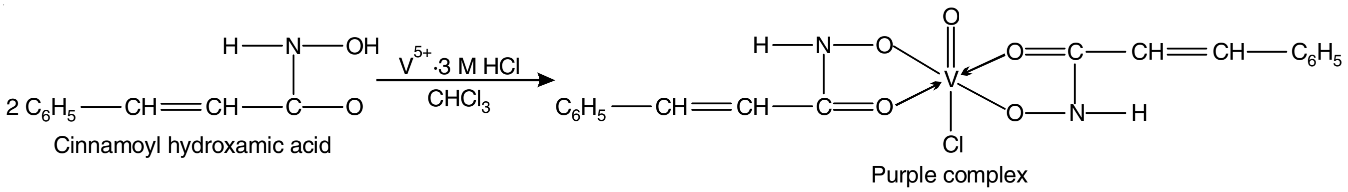
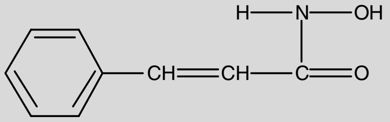


Fig. 2. Complexation of metal ion [vanadium(V)] with cinnamo hydroxamic acid (CHA)

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF COMPOUND (**1a**)

Comp. No.	Structure (IUPAC)	m.f.	m.w.	m.p. (°C)	Yield (%)
1a	 Cinnamoyl hydroxamic acid	$C_9H_9NO_2$	163.17	92	75.5

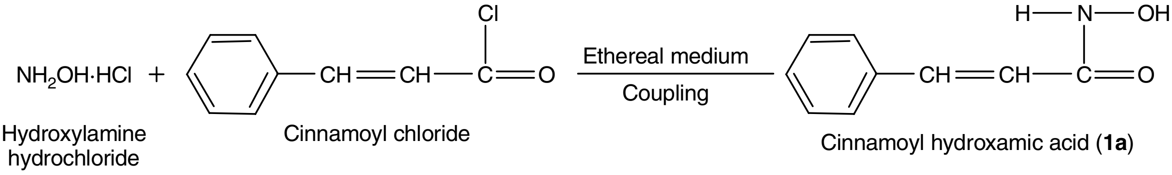


Fig. 3. Synthesis of unsubstituted cinnamo hydroxamic acid (**1a**)

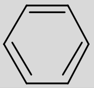
method. ^{1}H NMR spectrum of the compounds were carried out using Bruker Advance 400 MHz spectrometer at SAIF Panjab University Chandigarh. The solvent used was $CDCl_3$ and DMSO. IR spectra were recorded on a FTIR 390/2014/0514/290514 at Gujarat University Ahmedabad, India.

Synthesis of unsubstituted cinnamoyl hydroxamic acid (1a): The mixture of fine powered hydroxylamine hydrochloride (0.05 M) has been coupled with cinnamoyl chloride (0.05 M) in the presence of saturated aqueous solution of Na_2CO_3 (0.05 M) in 25 mL ethereal medium on constant stirring magnetic stirrer. 0 °C maintained during reaction. The compound precipitate out (yield 80 %), washed with water and then recrystallized with ethyl acetate (Table-1, Fig. 3).

RESULTS AND DISCUSSION

These compounds are synthesize by the coupling reaction between unsubstituted hydroxylamine and cinnamoyl chloride the reaction is carried out 0-5 °C keep constant of all reaction and characterized by ^{1}H NMR and IR spectroscopy. The important chemical shifts for the cinnamoyl hydroxamic acid (CHA) is given in the Table-2.

TABLE-2
^{1}H NMR DATA OF CINNAMOYL HYDROXAMIC ACID (**1a**)

S. No.	Signal (cps)	Chemical shift (t)	Multiplicity	Assigned group
1	250	2.50	Singlet	H-N-
2	108	10.80	Singlet	-OH
3	650	6.50	Doublet	=CH
4	34	3.40	Singlet	CH=
5	756	7.56	Doublet	

IR spectrum of cinnamoyl hydroxamic acid (1a): IR (KBr, ν_{max}, cm^{-1}): N-H stretching(3260), O-H stretching(3031), C-H stretching (2731), C=O stretching (1631), C=C stretching (1573), C-N stretching (1493), C-N stretching (1446), C-H bending (1352), C-H bending (1334), N-H bending (1067), N-O stretching (999), C-C-C stretching (853), C-H rocking (759), C-H rocking (707), C-H twisting (571), C-H twisting (515).

Spectrophotometrically determination of vanadium(V) using cinnamoyl hydroxamic acid as reagent: Simple, selective and sensitive spectrophotometric method has been developed for determination of vanadium(V) using cinnamoyl hydroxamic acid as reagent. This method is based on the formation of the purple colored radical cation on complexion reaction of vanadium(V) with cinnamoyl hydroxamic acid in 3 M hydrochloric acidic medium at pH 2.5 with their absorbance maximum at 460 nm (Table-3, Fig. 4). Beer's law is valid over the concentration range of 0.2-10.0 µg/mL with molar absorptivity and Sandell's sensitivity values as 5.69 × 10^4 mol^{-1} cm^{-1} and 0.0011 µg cm^{-2}, respectively. The proposed method has been successesfully applied for the analysis of vanadium(V) in water and soil samples. The precision, inwards of RSD of system is ± 0.99. The method is highly selective as most of the common ion and foreign ion do not interfere in the determination of vanadium(V) effect of acidity range.

TABLE-3
ABSORPTION SPECTRA OF VANADIUM(V) WITH CINNAMOYL HYDROXAMIC ACID IN AQUEOUS MEDIUM

S. No.	Wavelength (nm)	Absorbance
1	440	0.212
2	450	0.215
3	460	0.218
4	470	0.217
5	480	0.216
6	490	0.210
7	500	0.207

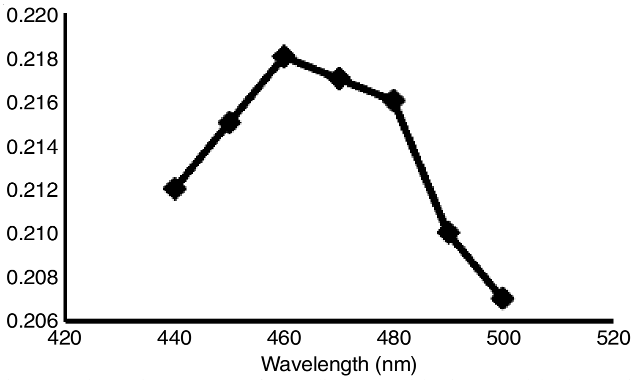


Fig. 4. Absorption spectra of vanadium(V) with cinnamoyl hydroxamic acid in aqueous medium

Absorption spectra: The absorption spectra of the complex vanadium(V) with cinnamoyl hydroxamic acid formed in aqueous solution against the reagent blank, exhibited the wavelength of maximum absorbance around 460 nm since the reagent blank has the negligible absorbance at this wavelength. It was used as reference for all further measurements (Table-3, Fig. 4).

Beer's law and calibration curve: The calibration curve was obtained from 0.2-10 ppm μg/mL of vanadium(V) using 3 M hydrochloric acid at a 460 nm. The proposed concentration range correlation coefficient of ± 0.99 (Table-4, Fig. 5). The detection limit D_L and quantitation limit Q_L of the method is 0.11 μg/mL and 0.43 μg/mL vanadium(V) in aqueous medium.

TABLE-4
ADHERANCE TO BEER'S LAW FOR THE DETERMINATION OF VANADIUM(V) USING CINNAMOYL HYDROXAMIC ACID*

Vanadium in aqueous medium (μg/mL)	Absorbance	Vanadium in aqueous medium (μg/mL)	Absorbance
0.2	0.115	5.4	0.481
0.6	0.122	6.2	0.557
1.0	0.140	7.0	0.670
1.4	0.167	7.8	0.820
1.8	0.212	8.4	0.870
2.4	0.250	9.2	0.957
3.0	0.310	10.0	0.960
3.8	0.355	10.8	0.961
4.6	0.440		

*Correlation ± 0.99

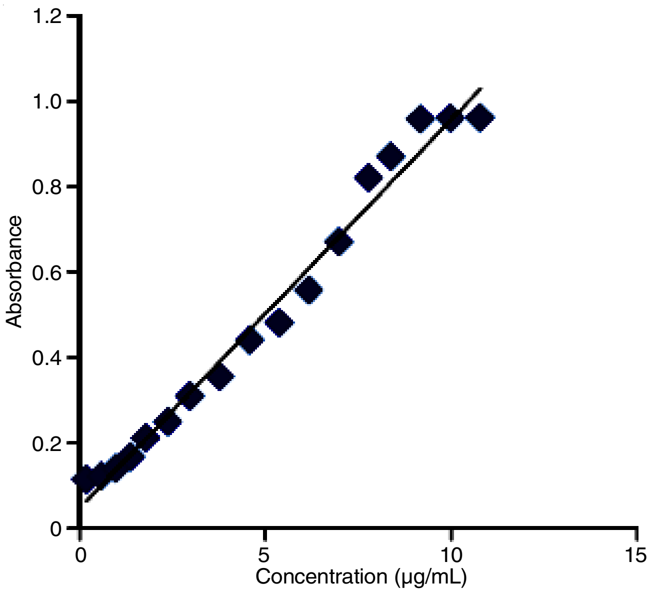


Fig. 5. Calibration curve for the determination of vanadium(V) with cinnamoyl hydroxamic acid in aqueous medium

Statistical data and precision: The precision of the method was determined by taking 7 replicates measurements each containing 11.74 μg of vanadium(V) per 25 mL of aqueous solution. The mean absorbance value was found to be 0.410 and standard deviation value ± 0.002 was obtained and relative standard deviation of ± 0.48 results shown in Table-5.

TABLE-5
STATISTICAL DATA AND PRECISION

Number of observation	Absorbance	Mean absorbance	Standard deviation	Relative standard deviation
N = 7	0.412 0.414 0.411 0.408 0.410 0.407 0.412	0.410	± 0.002	± 0.48

Effect of not target species: The influence of various species was investigated on the determination of vanadium(V) 11.74 μg/25 mL of (V) under optimum conditions. The limit was taken as the maximum concentration of the foreign ion causing a relative error of less than ± 1 %.The results are given in Table-6. Results show that NO_3^-, Sn^{2+}, PO_4^{3-}, Mo^{6+}, Co^{3+}, Bi^{3+}, Ba^{2+}, Fe^{3+}, BO_3^{3-} show positive interference.

TABLE-6
EFFECT OF NON TARGET SPECIES IN THE DETERMINATION OF VANADIUM(V) 6.5 × 10^{-4} M (10.60 μg/25 mL) FOR 8.5 × 10^{-2} M (CINNAMOYL HYDROXAMIC ACID), HCl 3 M AT 2.5 pH

Ions	Absorbance	Effect	Ions	Absorbance	Effect
Mn^{2+}	2200	No interference	NO_3^-	900*	Positive interference
Cu^{2+}	1800		Sn^{2+}	400*	
Cd^{2+}	1150		PO_4^{3-}	850*	
Al^{3+}	2400		Mo^{6+}	600*	
Pb^{2+}	2250		Co^{3+}	950*	
Ni^{2+}	2100		Bi^{3+}	500*	
Cr^{3+}	2350		Ba^{2+}	600*	
CH_3COO^-	1500		Fe^{3+}	700*	
SO_4^{2-}	1200		BO_3^{3-}	400*	

Application of the proposed method: The present method was satisfactory applied for the determination of vanadium(V) in polluted water and soil samples (industrial area of Siltara, Raipur) using calibration graph.

Determination of vanadium(V) in polluted water each filtered water sample 100 mL (industrial area of Siltara, Raipur, India) was evaporated nearly to dryness with a mixture of 1 mL of concentrated H_2SO_4 and 5 mL concentrated HNO_3 in a fume cupboard and was then cooled and neutralized with dilute NH_4OH in presence of 1-2 mL of 0.01% of tartrate solution. The resulted solution was then transferred in to a 25 mL calibrated flask and make up to the mark with distilled water. A 1 mL of this preconcentrared water sample was transferred in to 10 mL calibrated flask and the vanadium content was determined as described under procedure using masking agent [23]. The results are shown in Table-7.

Determination of vanadium(V) in polluted soil: An air-dried homonized soil sample 1 g (industrial area of Siltara, Raipur) was weighed accurately and placed in a 100 mL Kjeldahl flask. The sample was digested in the presence of an oxidizing agent following the method recommended. The content of flask was filtered through a Whatman filter paper No. 42, in to a 25 mL calibrated flask and neutralized with dilute ammonia in the presence of 1-2 mL of 0.01 % tartrate solution. It was diluted to the make with distilled water. 1-2 mL of the this solution was pipette in to a 10 mL calibrated flask and analyzed for vanadium content amount of vanadium(V) added then analyzed by the proposed procedure [24]. The results are summarized in Table-8.

TABLE-7
DETERMINATION OF VANADIUM(V) IN POLLUTED WATER

Sample	Vanadium originally found (µg/mL)	Vanadium added found (µg/mL)	Vanadium found (µg/mL ± SD)	Relative error	Recovery (%)
Polluted water	7.62	–	7.67 ± 0.05	± 0.22	98.75
	7.12	–	7.10 ± 0.04	± 0.14	99.00

TABLE-8
DETERMINATION OF VANADIUM(V) IN POLLUTED SOIL. MEAN ± STANDARD DEVIATION (n = 5)

Sample	Vanadium originally found (µg/mL)	Vanadium added found (µg/mL)	Vanadium found (µg/mL ± SD)	Relative error	Recovery (%)
Polluted soil	–	2.0	1.97 ± 0.05	± 0.17	98.50
	–	4.0	3.95 ± 0.02	± 0.22	98.75

Conclusion

Cinnamoyl hydroxamic acids were prepared. This compound is synthesized by the coupling reaction between hydroxylamine and cinnamoyl chloride the reaction is carried out 0-5 °C keep over reaction and characterized by ^{1}H NMR (Table-2) and IR spectrum. The coupling reagents employed in the present's methods *i.e.* cinnamoyl hydroxamic acid is sensitive and selective spectrophotometric reagents for the determination of vanadium(V) in water and soil samples (Industrial area of Siltara (Raipur)) with good results. The detection limit and quantitation limit is 0.11 µg/mL and 0.43 µg/mL, respectively.

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