

Synthesis and Analytical Applications of Hydroxamic Acids for Determination of Vanadium(V)

¹M. RASUL JAN*, ²NAZIR JAN AND ²MAHMOOD A KHAWAJA
¹Department of Chemistry, University of Peshawar, Peshawar, Pakistan
²PCSIR Laboratories, Peshawar, Pakistan

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Summary: A number of monohydroxamic acids like salicyl, cinnamo, m-nitro benzo, tartaric and benzohydroxamic acids as well as dihydroxamic acids were synthesized and characterized using spectroscopic techniques with the aim to develop selective chelating agents for determination of transition metals. Optimum conditions for maximum complexation and wavelength for spectrophotometric determination were investigated. λ_{max} of 308 \pm 2 was observed with all ligands investigated, while pH-2 and 11 were found optimum pHs for maximum complexation. Interferences effect of selected cations on determination of vanadium(V) and its detection limits were also investigated.

Introduction

Hydroxamic acids are colorless crystalline, weakly acidic compounds, which form metal complexes by chelation of metal ion between the two oxygen atoms of the monoanion to give a five membered ring. They are well known to form both soluble and insoluble colored complexes [1,2] and are thus useful as metal deactivators. The ability of hydroxamic acids to form stable transition metal complexes [3] is the basis of their usefulness as an analytical reagent [4,5]. This is the reason why hydroxamic acids have been used as chelating agents for the determination of metals in the samples of environmental and industrial importance [6,7]. Heavy metal determination at trace level has received special attention worldwide, because of health reasons, in different samples of environmental and industrial importance.

Hydroxamic acids have been used for the solid phase extraction of trace metals [8] and as a ligand has been incorporated into nitron film electrodes [9]. Hydroxamic acids have been also used for spectrophotometric determination of molybdenum [10]. The present method investigated, based on hydroxamic acid is not only more sensitive than the existing spectrophotometric methods but is quite simple and less time consuming and is more suited for interferences free matrices.

Results and Discussion

A number of mono hydroxamic acids like salicyl, m-nitrobenzo, benzo and tartaric as well as dihydroxamic acids, like phthalic, succinic and oxalic dihydroxamic acids were synthesized and characterized using spectroscopic techniques [11]. The reactivity of these acids were checked with various metals like Mn(II), Co(II), Pb(II), Cu(II), Cd(II), Ni(II), Fe(II), Cr(VI), V(V) and Mo(VI). It was observed that Mo(VI) and V(V) react easily with salicyl, m-nitrobenzo, cinnamo and benzo hydroxamic acids. After preliminary investigation, these ligands were chosen for the spectrophotometric determination of vanadium.

For the determination of V(V) using salicyl (SHA), m-nitrobenzo (m-N-BHA), cinamo (CHA) and benzohydroxamic acids (BHA) as chelating agents, optimum wavelength were investigated and the results are shown in Fig. 1. It can be seen from the figure that 308.2 nm was found to be the most suitable wavelength for V(V) determination using these chelating agents. The results of pH optimization are shown in Figure 2. It was observed from the figure that pH 2, 11, and 11 were found to be the optimum pH for V(V)-SHA, V(V)-m-N-BHA, V(V)-CHA and V(V)-BHA complexation respectively.

A spectrophotometric study for the determination of molecular formula and stability

*To whom all correspondence should be addressed.

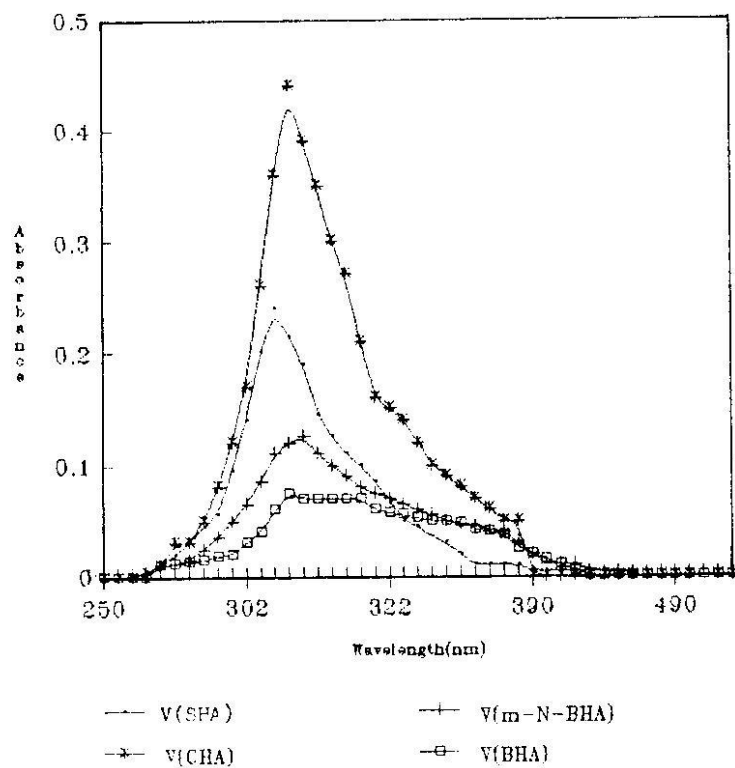


Fig. 1: Absorbance of V(v) complexes with hydroxamic acids as function of wavelength

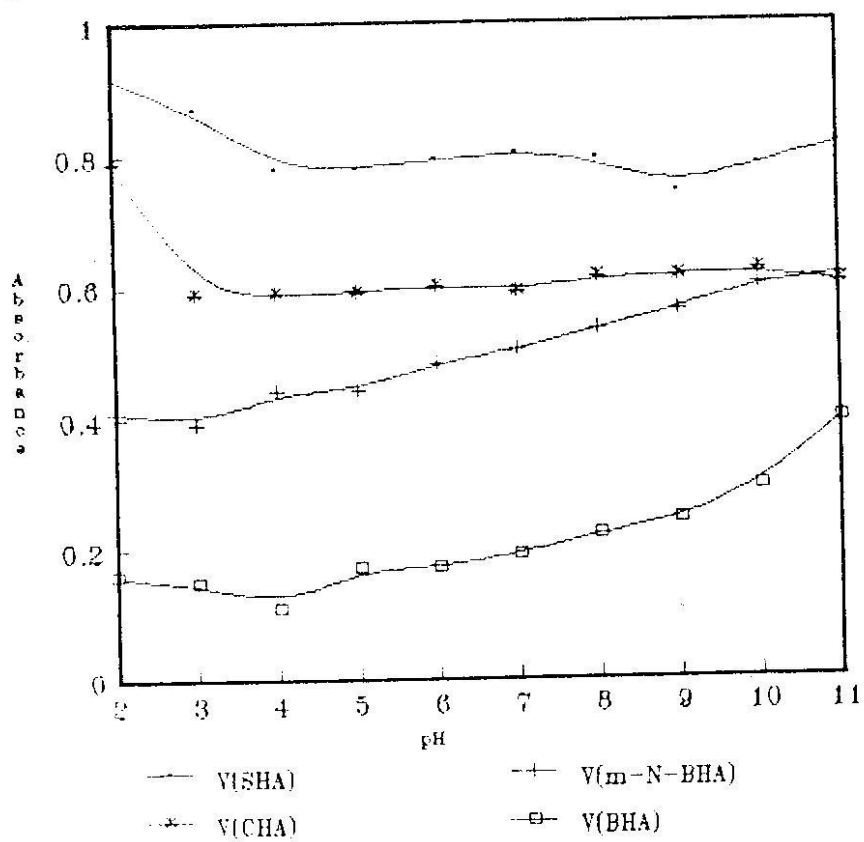


Fig. 2: Effect of pH on the absorbance of V(v) complexes with different hydroxamic acids.

constant of V(V)-hydroxyamic acid was carried out in aqueous solution using continuous variation method with the following formula.

$$K_f = \frac{[MX]}{[M][X]}$$

where

MX = Concentration of complex.

[M] = Concentration of free metal ion and

[X] = Concentration of free ligand.

These investigation revealed that the ratio of metal ligand is 1:1 indicating ML type of complexes. The results of stability constants are given in Table-1, and are 1.5×10^5 , 2.45×10^5 , 6.86×10^5 and 8.1×10^4 for the complexes of SHA, m-BHA, CHA and BHA with V(V) respectively. It can be infer red from these values that all hydroxamic acids form complexes of the same stability with V(V).

Table-1: Stability constant for V(V) with various hydroxamic acid

Metal Complex	Stability Constant
V(SHA)	1.56×10^5
V(m-N-BHA)	2.45×10^5
V(CHA)	6.86×10^5
V(BHA)	8.1×10^4

The interference studies of various cations like Cd(II), Cu(II), Zn(II), Pb(II), Ni(II), Co(II), Fe(II), Mn(II), Mo(VI) and Cr(VI) were investigated on determination of V(V) using SHA m-N-BHA, CHA, and BHA as chelating agents. The results are given in Table-2. It was observed that none of the metals investigated upto equimolar and higher concentrations using SHA and CHA as chelating agent interfered. It was further observed that while using m-N-BHA as chelating agent only Cu(II) and Fe(II) interfered and reduced the absorbance signal drastically. The decrease in the absorbance could be due to the stable chelate formation of Cu(II) and F(II) with the ligand which may have absorbance characteristics different from that of vanadium complex. Using benzohydroxamic acid as chelating

Table-2: The inference of various cations on Vanadium(V) determination using hydroxamic acids as chromogenic reagents.

Conc. of V(V) (ppm)	10	10	10	10	10	10	10	10	10	10	10
Amount of cations added (ppm)	0	2	4	6	8	10	12	14	16	18	20
Recovery of V(m-N-BHA) % in the presence of Fe(II)	100.00	32.87	46.57	57.53	65.75	72.60	79.45	87.67	94.45	101.36	132.73
Recovery of V(m-N-BHA) % in the presence of Cu(II)	100.00	21.91	31.50	30.13	31.50	31.50	31.50	31.50	31.50	31.50	31.50
Recovery of V(BHA) % in the presence of Fe(II)	100.00	117.77	128.88	137.77	148.88	164.44	177.77	188.88	196.77	200.36	205.35
Recovery of V(BHA) % in the presence of Cr(VI)	100.00	106.97	104.65	104.65	103.48	106.97	109.30	112.48	116.50	118.25	128.33
Recovery of V(BHA) % in the presence of Mo(VI)	100.00	96.04	75.58	69.78	86.04	90.13	90.13	90.13	90.13	90.13	90.13
Recovery of V(BHA) % in the presence of Pb(II)	100.00	122.22	131.11	137.77	131.11	117.77	111.11	106.66	97.77	97.77	97.77
Recovery of V(BHA) % in the presence of Ni(II)	100.00	108.88	113.33	120.00	124.44	126.66	128.88	131.11	134.25	138.50	143.11
Recovery of V(BHA) % in the presence of Co(II)	100.00	122.22	131.11	142.22	146.66	154.44	160.00	166.66	172.44	178.00	178.00
Recovery of V(BHA) % in the presence of Zn(II)	100.00	111.62	113.95	111.95	109.32	103.48	95.25	91.36	88.23	85.36	82.35
Recovery of V(BHA) % in the presence of Mn(II)	100.00	117.77	121.11	111.11	95.55	71.11	55.55	44.45	32.35	26.36	24.45
Recovery of V(BHA) % in the presence of Cd(II)	100.00	96.51	95.34	97.67	76.74	72.00	67.34	63.22	60.09	55.55	50.14

Conditions:

Ligands	=	SHA	m-N-BHA	CHA	BHA
λ_{max}	=	310 nm	310 nm	308 nm	308 nm
Buffers pH	=	2	11	2	11

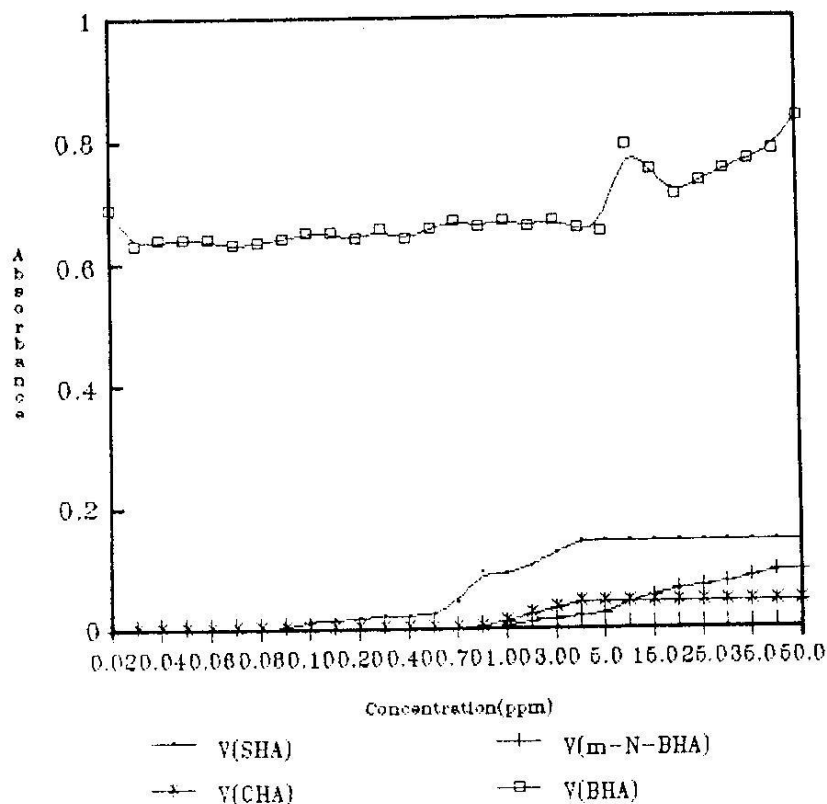


Fig. 3: Absorbance of V(v) complexes using different hydroxamic acids as function of V(v) concentration.

agent, Mo(VI), Ni(II), Fe(II), Co(II) and Cr(VI) were found to be the serious interferant, while the presence of Cd(II) did not pose much problems. Zn(II), Pb(II) and Mn(II) caused enhancement in the absorbance with concentration upto 6 ppm but beyond that level, further increase in the concentration of interferant cations caused a decrease in the absorbance reading. This could be due to the reason that in the beginning, these interfering cations compete with V(V) for benzohydroxamic acid complexation and then after certain level of complexation, these interfering cations start reacting with VO_3 anion and thus make the V^{+5} unavailable for complexation. This lead to decrease in the absorbance. The presence of Mo(VI) and Cu(II) caused negative interferences.

Absorbance at very small concentration of V(V) was observed only for V(V) SHA and from the effect of absorbance behaviour on concentration, detection limit was evaluated and it, 0.1 ppm by

using SHA as chelating agent. This suggest that the method is quite sensitive for determination of V(V). For pre-concentration aimed at better detection limit, a number of organic solvents were investigated to find out the efficiency of extraction into organic phase (Table-3). Among the solvents investigated non was found suitable for extraction.

Experimental

Apparatus

A double beam spectrophotometer, UV-200S Shimadzu and WPA CCD 660, pH meter were used throughout this work.

Reagents

All reagents used, except the hydroxamic acids were of analytical grade purity (BDH). Hydroxamic acids were synthesized in our own laboratory according to the standard procedure [12].

Table-3: Extraction of V(V) complexes using hydroxamic acids in different diluents

Diluent	V(SHA)		V(m-N-BHA)		V(CHA)		V(BHA)	
	Org.phase	Aq.phase	Org.phase	Aq.phase	Org.phase	Aq.phase	Org.phase	Aq.phase
Chloroform	0.25	0.86	1.10	0.48	1.15	0.85	1.00	0.56
Iso butyl alcohol	1.24	0.58	No separation		No separation		0.19	0.54
Amyl acetate	1.11	0.94	1.14	0.38	1.14	0.74	0.31	0.12
n-butanol	1.38	0.64	No separation		1.10	0.19	No separation	
Benzene	1.50	0.98	0.31	0.52	0.48	0.56	0.58	0.62
Diethyl ether	No separation		No separation		No separation		No separation	

Conditions:

Ligand	=	SHA	m-N-BHA	SHA	BHA
λ_{\max}	=	310 nm	310 nm	308 nm	308 nm
Buffer pH	=	2	11	2	11

1. Buffer Solutions

Briton Robinson buffer of pH range 2-11 were prepared according to the standard method [13].

2. Metal Stock Solution

100 ppm stock solution of the metal V(V) was prepared by dissolving an appropriate amount of ammonium metavanadate in distilled water. Dilution was made with double distilled water. Dilute solutions were prepared fresh every day from the stock solution.

3. Ligand Solution

0.1% of the ligands salicyl, m-nitrobenzo, cinnamo and benzo hydroxamic acid solutions were prepared by dissolving 0.1 gram of respective ligand in 100 ml distilled water.

Procedure

As a preliminary check, 1 ml of the ligand solution (0.1%) and 1 ml of the metal solution (100 ppm) were mixed, by observing change in colour on mixing the formation of metal ligand complex was confirmed and these solutions were monitored in the range of 250-500 nm for wavelength optimization studies. For the determination of suitable pH for complexation, the amount of metal and ligand was kept constant in solution, while pH was varied by addition of Briton Robinson buffer (10 ml) in the range of 2-11. Interference studies were conducted at optimum pH at different concentration, while for determination of detection limit and linearity of the method working standards in the range of 5 ppb to 80 ppm were investigated at optimum pH. The absorbance of each solution was measured at optimum wavelength after half an hour equilibration time. For pre-concentration and trace determination purpose, 50 ml of the aqueous solution of metal chelate was extracted with 10 ml of the organic

phase using separatory funnel after proper mixing and giving 10 minutes equilibration time. The absorbance readings of both phases were noted at optimum wavelength.

Conclusion

All the synthesized hydroxamic acid were found to react with V(V) giving λ_{\max} in the range of 308 ± 2 nm. While optimum pH for complexation was observed to be 2 and 11. All these ligands were found to be non specific as most of the diverse cations investigated showed either additive or negative interferences. The method is sensitive, quite good for simple matrices, however for complex matrices prior removal of the interferent cations would be essential.

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