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Application of *p*-Substituted Cinnamohydroxamic Acids to the Spectrophotometric Determination of Molybdenum(VI)

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The formation of greenish yellow coloured complex of molybdenum(VI) with nine new *p*-substituted cinnamohydroxamic acids have been studied. This study shows that the molybdenum complex of nine new hydroxamic acids have molar absorptivities between 3.5×10^4 and 1.1×10^5 l mol⁻¹ cm⁻¹. This value is considerably large as compared to value obtained by benzohydroxamic acid, *N*-phenylbenzohydroxamic acid and *N*-*p*-chlorophenylbenzohydroxamic acid^{1,2}. A rapid extraction and spectrophotometric method for the determination of molybdenum is described, employing the most promising of these reagents, *N*-*p*-tolyl-*p*-methoxycinnamohydroxamic acid.

INTRODUCTION

Hydroxamic acids have been widely used as selective and sensitive reagents for solvent extraction and spectrophotometric determination of various metal ions viz. cerium^{3,4}, niobium⁵, titanium^{5,6}, uranium^{7,8}, vanadium⁹⁻¹² etc. A few hydroxamic acids have been used for the solvent extraction and spectrophotometric determination of molybdenum¹³⁻²⁰. Rowland and Meloan¹³ reported that molybdenum(VI) forms a orange yellow 1 : 2 chelate with nicotino hydroxamic acid at pH = 3.0. The absorbance maxima is at 350 nm and the chelate has a molar absorptivity of 1.6×10^3 l mole⁻¹ cm⁻¹. Uranium and titanium interfere at all concentration levels. Agrawal^{1,14} has examined that benzohydroxamic acid gives a greenish yellow coloured complex with molybdenum(VI) at pH = 2.0—3.0 and vanadium, cerium, titanium, iron are interfering. Mikulaj¹⁵ have reported solvent extraction of activated molybdenum with *N*-phenylbenzohydroxamic acid. Salicylo hydroxamic acids¹⁶⁻¹⁸ and *N*-*o*-tolyl-*o*-methoxybenzohydroxamic acid¹⁹ have also been reported for extraction and spectrophotometric determination of molybdenum(VI) but all these acids are less selective and sensitive (Table I).

A review of the literature reveals that cinnamohydroxamic acids have not been used so far in the solvent extraction and spectrophotometric determination of molybdenum(VI). It has been found that substituted cinnamohydroxamic acids are more selective and sensitive than other reported hydroxamic acids. In the present investigation nine *p*-substituted cinnamohydroxamic acids^{20,21} have been studied for the spectrophotometric determination of mo-

TABLE I

Comparison of Spectrophotometric Methods for the Determination of Molybdenum

Hydroxamic acid	Colour of the complex	Solvent	pH/acidity	λ_{\max} nm	$\frac{\epsilon}{1 \text{ mol}^{-1} \text{ cm}^{-1}}$	Interference	Ref.
Nicotino-	OY	1-Hexanol	3.0	350	1.6×10^3	$\text{U}^{+6}, \text{Ti}^{+4}$	13
Benzo-	GY	1-Hexanol	2.0—3.0	370	2.2×10^3	$\text{V}^{+5}, \text{Ce}^{+4}, \text{Ti}^{+4}, \text{Fe}^{+3}$	1
	Y	—	1.2—3.6	350	1.2×10^4	$\text{V}^{+5}, \text{Ce}^{+4}, \text{Ti}^{+4}, \text{Fe}^{+3}$	
Salicylo-	Y	—	1.3	290	8.6×10^4	—	16
	Y	Isoamyl alcohol	2.5—3.0	345	9.0×10^3	$\text{Cr}^{+3}, \text{Fe}^{+3}, \text{V}^{+5}$	17
	Y	—	6.3—7.02	410—440	—	—	18
<i>N</i> - <i>o</i> -Tolyl- <i>o</i> -methoxybenzo-	Y	Isoamyl alcohol	1.0—2.5	350	9.1×10^3	—	19
<i>N</i> - <i>p</i> -Tolyl- <i>p</i> -methoxycinnamo-	GY	Chloroform	4—8M HCl	390	1.1×10^5	$\text{V}^{+5}, \text{Ti}^{+4}$	—

OY = Orange Yellow, GY = Greenish Yellow, Y = Yellow

lybdenum in trace levels. The *N*-*p*-tolyl-*p*-methoxycinnamohydroxamic acid is shown to be most selective and sensitive reagents, surpassing the BHA, PBHA, *p*-Cl-BHA and other reported hydroxamic acids. It gives an intense greenish yellow coloured complex in the molybdenum (extracted with chloroform from 4—8 M HCl) molar absorptivity being $1.1 \times 10^5 \text{ l mole}^{-1} \text{ cm}^{-1}$. The effect of various parameters viz. acidity, reagent concentration, solvents and diverse ions on the absorbance of the molybdenum complex system have been studied.

EXPERIMENTAL

All the chemicals used were of G. R., E. Merck grade. The preparation and properties of the hydroxamic acids were described elsewhere^{20,21}.

A 0.01 M solution of the reagent in ethanol free chloroform, was used for all extraction purposes.

A standard solution of molybdenum was prepared by dissolving requisite amount of ammonium molybdate $(\text{NH}_4)_6\text{MO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in distilled water and standardised volumetrically²².

Absorbance measurements were made on a VSU2-P spectrophotometer.

Procedure

Transfer an aliquot of molybdenum solution (12.5 ppm) to a separatory funnel and adjust the acidity at 6 M with concentrated hydrochloric acid and distilled water to a final volume of 20 ml. Then add 5 ml of *N*-*p*-tolyl-*p*-methoxycinnamohydroxamic acid (0.01 M in chloroform). Shake the contents vigorously for 2—5 min and allow the phases to separate. Collect the greenish yellow chloroform layer in a 25 ml volumetric flask after passing through anhydrous sodium sulphate. Wash the aqueous phase with 5 ml chloroform. Repeat the extraction with 5 ml of the reagent solution to ensure the complete recovery of molybdenum. Finally, dilute the combined extract

up to the mark with the chloroform and measure the absorbance at 390 nm against reagent blank.

RESULTS AND DISCUSSION

Chloroform solution of *N-p*-Tolyl-*p*-methoxycinnamohydroxamic acid (*N-p*-T-MeCHA) forms a greenish yellow coloured complex with molybdenum(VI) from 4—8 M hydrochloric acid. The greenish yellow complex of molybdenum with *N-p*-T-MeCHA has a general absorption spectra (between 300—600 nm) and obeys Beer's law at 390 nm. Therefore, all the measurements are made at this wavelength. Spectral characteristic of molybdenum coloured system is given in Table II. The analytical data for the extraction of molybdenum(VI) are given in Table III and IV.

TABLE II

Spectral Characteristic of Molybdenum(VI) N-p-Substituted Cinnamohydroxamic Acids

Molybdenum	= 12.5 $\mu\text{g}/25$ ml
Molarity	= 6 M HCl
Colour Chloroform extract	= Greenish Yellow
λ_{max}	= 390 nm

Cinnamohydroxamic acid	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$
<i>N</i> -Phenyl-	4.3×10^4
<i>N-p</i> -Tolyl-	3.5×10^4
<i>N-p</i> -Chlorophenyl-	3.7×10^4
<i>N-p</i> -Tolyl- <i>p</i> -methoxy-	1.1×10^5
<i>N-p</i> -Chlorophenyl- <i>p</i> -methoxy-	7.9×10^4
<i>N</i> -Phenyl- <i>p</i> -chloro-	5.9×10^4
<i>N-m</i> -Tolyl- <i>p</i> -Chloro-	6.7×10^4
<i>N-p</i> -Tolyl- <i>p</i> -Chloro-	7.0×10^4
<i>N-p</i> -Chlorophenyl- <i>p</i> -Chloro-	5.9×10^4

Beer's Law

The greenish yellow coloured Mo(VI) complex adheres to Beer's law in the range of 0.05—1.0 ppm of molybdenum. The molar absorptivity is 1.1×10^5 $1 \text{ mol}^{-1} \text{ cm}^{-1}$ at 390 nm.

Effect of Acidity

The optimum acidity range for the formation of greenish yellow coloured complex was found to be 4—8 M hydrochloric acid. The absorbance of the complex decreased above or below this range.

Effect of Reagent Concentration

The effect of reagent concentration has been investigated by measuring the absorbance at 390 nm of solution containing 12.5 μg Mo/25 ml and varying

TABLE III

Effect of Molarity of Hydrochloric Acid on the Extraction of Molybdenum with N-p-Tolyl-p-Methoxycinnamohydroxamic Acid

Molybdenum = 12.5 μg /25 ml of Chloroform

λ_{max} = 390 nm

Conc. of HCl/M	% E	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$
2.0	89	1.0×10^5
4.0	100	1.1×10^5
5.0	100	1.1×10^5
6.0	100	1.1×10^5
7.0	100	1.1×10^5
8.0	100	1.1×10^5

TABLE IV

Effect of Ammonium Thiocyanate on the Extraction of Molybdenum with N-p-Tolyl-p-Methoxycinnamohydroxamic Acid

Molybdenum = 12.5 μg /25 ml of Chloroform

λ_{max} = 390 nm

Molarity = 6 M HCl

Conc. of NH_4SCN mg/ml	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$
91.4	1.5×10^5
182.7	1.5×10^5
274.1	1.7×10^5
319.7	1.8×10^5
365.4	1.8×10^5
411.1	1.8×10^5
456.8	1.6×10^5

the amount of reagent. It is found that the maximum colour formation takes place with 5 ml of 0.01 M reagent solution in chloroform. The extraction is incomplete with less reagent concentration. Excess of the reagent could be used and has no effect on the intensity of the complex.

Shaking Time and Stability of Complex

Extraction of molybdenum is very rapid under the conditions recommended in the procedure. Shaking for 2—5 min was enough to attain the equilibrium. The complex is stable for several hours under the optimum conditions. The absorbance remains unchanged for several hours.

Effect of Ammonium Thiocyanate

The effect of ammonium thiocyanate on the extraction and spectrophotometric determination of molybdenum(VI) has been studied. There is no change in the absorption spectrum on addition of ammonium thiocyanate except the intensity of the colour increases. The results indicate that 319.7—411.1 mg/ml of ammonium thiocyanate is maximum to increase the molar absorptivity of the molybdenum(VI) complex from 1.1×10^5 to 1.8×10^5 l mol⁻¹ cm⁻¹. Excess of ammonium thiocyanate decreases the molar absorptivity (Table IV).

Stoichiometry of the Complex

Job's method of continuous variation²³ and molar ratio method²⁴ was applied to study the stoichiometry of the molybdenum hydroxamate complex. The results indicate ratio of metal to ligand is 1 : 2.

Effect of Diverse Ions

The recommended procedure was followed to study the interference due to various ions in the direct spectrophotometric determination of molybdenum with *N-p-T-p-MeCHA*. Moderate amounts of many commonly associated ions with molybdenum were tolerated. The molybdenum (12.5 µg/25 ml) was determined in presence of Cu⁺² (65 mg); Co⁺² (65 mg); Ni⁺² (50 mg); Be²⁺ (50 mg); Ce⁺⁴ (40 mg); Al⁺³ (40 mg); As⁺³ (40 mg); Cd⁺² (40 mg); Ga⁺³ (50 mg); Ge⁺⁴ (50 mg); Hg⁺² (40 mg); NH₄⁺ (50 mg); Mg⁺² (50 mg); Mn⁺² (35 mg); Pb⁺² (35 mg); Zn⁺² (35 mg); Zr⁺⁴ (35 mg); Sn⁺² (35 mg); UO₂⁺² (30 mg); Ca⁺² (80 mg). The V⁺⁵ and Ti⁺⁴ showing strong interference. The interference of vanadium and titanium was eliminated by reducing vanadium with ferrous sulphate and titanium by masking with sodium fluoride. Similarly the anions viz. NO₂⁻ (40 mg); F⁻ (50 mg); Cl⁻ (40 mg); Br⁻ (40 mg); I⁻ (40 mg); oxalate (20 mg); tartrate (20 mg); phosphate (40 mg); citrate (20 mg); borate (20 mg) are not interfering.

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SAŽETAK

Primjena *p*-supstituiranih cinamohidroksamnih kiselina za spektrofotometrijsko određivanje molibdena(VI)

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Studirano je nastajanje zelenkasto-žuto obojenih kompleksa molibdena(VI) sa devet novih *p*-supstituiranih cinamohidroksamnih kiselina. Ti kompleksi imaju molarni apsorpcioni koeficijent između 3.5×10^4 i 1.1×10^5 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$.

Opisana je ekstrakcija i spektrofotometrijska metoda za određivanje molibdena primjenom najpogodnijeg reagensa, *N-p*-tolil-*p*-metoksicinamohidroksamne kiseline.

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