CHAPTER - II

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SPECTROPHOTOMETRIC DETERMINATION OF

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MOLYBDENUM (VI) WITH

3,5-DICHLORO SAT

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<u>SPECTROPHOTOMETRIC</u> <u>DETERMINATION</u> <u>OF</u> <u>MOLYBDENUM</u> (VI) <u>WITH</u> 3,5 - DICHLORO SALICYLALDEHYDE THIOSEMICARBAZONE.

INTRODUCTION

Molybdenum is gray, heavy, hard and refractory metal which is useful principally in the targets of xray tubes and structural members in high vacuum tubes for electronic purposes because of the metals ability to form tight seals with glass. Molybdenum alloys are notable for their hardenability and toughness (which makes them useful for high speed tools, armor plates), for their corrosion resistance and strength at elevated temperatures (ferrous and nonferrous alloys). It also finds its way into important catalysts used in the petroleum and chemical industries, pigments, lubricants and fertilizers, components of radio tubes and more recently in jet engines.

The most stable oxidation states of the molybdenum are +3, +5 and +6. But +6 is the commonest oxidation state of molybdenum. As a trace element it is essential to the health of plant and probably of animals. During the past few years, the increasing use of molybdenum alloys in the electronics and other industries has magnified the need for simple and rapid method for the determination of molybdenum in a variety of materials.

Many reagents have been reported for the

photometric determination of molybdenum(VI) in the literature. A critical review has been given by Busev¹ and by Khosala et al². Despite of several disadvantages the classical thiocyanate method is frequently used as one of the most accurate spectrophotometric method for the determination of molybdenum $^{3-5}$. Improvements of thiocyanate method have also been reported in the literature $^{\rm 6-7}$. Many more recent reagents which form ternary complexes with molybdenum thiocyanate are used for the photometric determination of molybdenum. These reagents include Vanillin thiosemicarbazone⁸, methotrimeprazine⁹, N-hydroxy-N-p-chlorophenyl-N'-p-chlorophenylo-chlorobenzamide hydrochloride¹⁰, 4-acety1-2(acety1amino)-5-dimethyl- Δ^2 -1,3,4-thiadiazole¹¹, tri-n-octylamine¹². Some of the ternary complexes of the molybdenum which have been reported with those of the ligands in combination are such as 4-(2-pyridylazo) resorcinol(PAR) and hydroxylamine¹³, catechol violet and cetyltrimethyl ammonium bromide¹⁴, N-phenyl benzohydroxamic acid and phenyl fluorone¹⁵. However, some of these reagents possess disadvantages e.g :- With N-phenyl benzohydroxamic acid and phenyl fluorone, double extraction is necessary. These reagents are highly sensitive but suffer from interference of many metal ions.

Recently the various dyes are also proposed for the spectrophotometric determination of molybdenum. Some of those include monoazoderivatives of pyrogallol¹⁶, 2thiopyrogallol¹⁷, 5-Br-PADP¹⁸, galloycyanine¹⁹, 3,4-dihydroxyazobenzene²⁰ gallein²¹, catechol violet²², 4-(2thiazolylazo) catechol²³, phenyl fluorone²⁴, 2',3',4'trihydroxyazobenzene-4-sulphuric acid²⁵, 4-butyryl pyrogallol²⁶, 4-propionylpyrogallol²⁷, 4-galloyl pyrogallol²⁸, quinalizarin²⁹. Photometric determination of molybdenum in rocks and minerals using various amines have been reported in the literature which include : N-benzoyl-N-phenylhydroxyl amine³⁰, trioctyl or dinonyl amine³¹, N-(4-nitrocinnamoyl)-N-(4-chlorophenyl)hydroxyl amine³², tri-n-octyl amine³³. However, these reagents involve extractive procedure.

The complexes of molybdenum with various mixed ligands increases the selectivity and sensitivity of the determination along with the enhancement in the solubility in organic solvent and the extraction rate. Some of these mixed ligand includes : 2,7-dihydroxyfluorescein (DHF) and cetyltrimethyl ammonium bromide 34 , TBP and TOPO³⁵, malachite green and p-chloro mandelic acid³⁶ neotetrazolium chloride and thiocyanate³⁷, etc. By using these mixed ligands molybdenum is determined, present in alloys, steel, ores, river water and minerals. However, these ligands suffer from interferences of metal ions, masking agent is used to eliminate the interference of metal ions. Other numerous chelating agents are reported in the literature as sensitive reagents for determination of molybdenum. These reagents include :

hydroxamic acids : N,N'-diphenyl thiocarbamohydroxamic acid³⁸, 2-salicylidenimino benzohydroxamic acid³⁹, (2pyridinyl methylene)amino-2-benzohydroxamic acid⁴⁰, thiophene-2-hydroxamic acid(THA)⁴¹, tiron⁴, tris(2,6-dimethoxy phenyl phosphine)⁴², derivatives of thiosemicarbazone⁴³⁻⁴⁴, quinoline and its derivatives⁴⁵⁻⁴⁸, ketones⁴⁹⁻⁵¹ coumarines⁵², thiolig ands⁵³⁻⁵⁷, carbamates⁵⁸, 1,5-diphenyl carbazone⁵⁹, salicylaldehyde isonicotinoyl hydrazone⁶⁰, 1-nitroso-2-naphthol⁵¹, oximes⁶²⁻⁶⁶, imidoyl phenyl hydrazine⁶⁷, bromopyrogallol (I) and hexadecyltrimethyl ammonium (II)⁶⁸, etc.

However, the photometric methods based on these above reagents suffer from various difficulties e.g -With salicylaldoxime and salicylaldehyde thiosemicarbazone 30 mins waiting is required. These reagents have low selectivity, tedious operation and serious interference from ions commonly associated with the molybdenum such as V(IV), Cu(II), Ni(II), Cr(VI), Co, Bi, Ag, Ti(IV), Zr(IV), W(VI). Hence these methods are not suitable for routine analysis.

In the present method the proposed reagent 3,5dichloro SAT reacts with molybdenum in presence of stannous chloride in $3N H_2SO_4$ to form pink coloured complex. The absorbance of the complex is measured at 525nm against solvent blank. This method is free from the disadvantages mentioned earlier. The method is simple and sensitive.

A summary of the reagents reported for the determination of molybdenum (VI) describing the conditions, characteristics of the complex, interferences and special remarks is given in the Table No. 1.

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TABLE NO. 1 :- SUMMARY OF THE REAGENTS REPORTED FOR MO (VI)

	r			[Γ	
Sr. No.	Reagent	Conditions	λmax, Beer's Ra- nge Molar extin- ction coefficie- nt and Sensitiv- ty	Interfer- ence	Remarks	Ref. No.
1	2	3	4	5	6	7
1	Thiocyan- ate	Conc. HCl(5ml) Aq. ascorbic acid.	λmax = 465nm. upto 6 µg/ml	-	Waiting 7to 10 min. shaking 305, reagent bl- ank needed	6
2	Thiocyan- ate	10M HCl (1.2ml) (NH ₄) ₂ SO ₄ FeSO ₄ 6H ₂ O (1ml) in 0.1M H ₂ SO ₄ , Aq. 20% NH ₄ SCN (1ml) 20% SnCl ₂ (1ml) ethanol (10ml) + H ₂ O.	λmax = 465nm. upto 4 ppm S = 14 μg/cm ²	Oxalate and Re(VII) interfere	Shaking 1 min. Blank extr- act needed	7
3	Vanillin thiosemi- carbazone	HCl medium	$\lambda \max = 470 nm.$ 0.1-4.6 µg $\varepsilon = 19800$		1:4:2 comp- lex Mo det- ermined in steels.	8
4	Methotri- meprazine and thio- cyanate.	HCl medium	λmax = 465nm. 0.02-6 μg/ml € = 16000	-	Mo determi- ned in all- oy, steels and ores.	9
5	N-hydroxy -N-p-chl- orophenyl -o-chlor- obenzami- dine hyd- rochloride	0.75-4M HCl Ascorbic acid	$\lambda \max = 470 nm.$ 3 - 24 ppm $\varepsilon = 3300$ $S = 0.029 \mu g/cm^{2}$	_	Molybdenum determined in ores and steels.	10

1	2	3	4	5	6	7
6	4-acetyl- 2(acetyl- amino)-5- dimethyl- Δ^2 -1,3,4- thiadiaz- ole and thiocyan- ate.	HC1	λmax = 470nm. 0.06-2.5 ppm € = 20100	-	1:4:2 comp- lex Mo det- ermined su- ccessfully in Mo steel, complex is stable for 1 week at room temp.	11
7	Tri-n-oc- tyl amine and thio- cyanate.		$\lambda \max = 470 nm.$ 0.1 -2 ppm $\varepsilon = 26000$	-		12
8	4-(2-pyr- idylazo) resorcin- ol PAR & hydroxyl- amine.	0.1M tartaric acid(0.2ml), 0.05M DCTA (0.4ml), hydr- oxyl ammonium sulphate 100mg/ml(10ml), 0.001Maq. PAR (10ml), pH = 6 acetatebuffer (10ml).	}max = 530nm	Co and Fe interfere Mg amoun- ts of Ni, Cu, Zn & Th is masked.	1:1:1 comp- lex.Boiling 10 min. Reagent blank is needed.	13
9	Catechol Violet & cetyltri- methyl ammonium bromide.	pH = 3 to 5 (or ≌ 6)	λmax = 675 nm E = 46000, 9.6 to 96 ppm			14

1	2	3	4	5	6	7
10	N-phenyl benzohyd- roxamic acid(I) & phenyl flourone (II)	I) 3.5-6M HCl II) 0.25-0.3M HCl	λmax = 518 nm upto 0.6 ppm € = 74,000	Sodium metabisu- lphite is added to eliminate interfer- ence of V(IV) and (V) For Ti(IV) Oxalate ions is added	Successful determinat- ion of Molybdenum present in standard steel samp- le 1:2:1 complex.	15
11	4-(4-Ido- phenylazo) pyrogall- ol(I) and 4-(2,3,4- Trihydro-	I) For Mo(VI) I 5 to 70mM H_2SQ_4 , 3 to 4 fold molar excess of R(I)	λmax = 480 nm, 0.06 to 3.4ppm € = 37,500		1:2 complex	16
	xyphenyl- azo)-ben- zene sul- phuric acid(II).	II) For MoR II 5 to 100 <u>n</u> m H ₂ SO ₄ .	λmax = 460nm, 0.16 to 3.8ppm € = 20,500		1:2 complex	
12	2-Thiopy- ragallol.	1.2M-HCl, 0.5% aq. R (5ml)	$\lambda \max = 525 nm,$ 0.25 to 10ppm $\epsilon = 19,000$	W(VI) and Pd(II) interfere	Stability = 2h, Analysis of steel	17
13	NH ₂ OH-5- Br-PADP [2-(5-br- omo-2-py- ridylazo) -5-(diet- hylamino) phenol _J I)] + poly(e- thanediol octyl ph- nyl ether)		λmax = 600 to 605 nm upto 3 ppm € = 48,000	Be, Mg, Ca, Sr, Ba, U(VI) Mn(II), Fe(III), Co and Ni need masking	1:1:1 Complex	18

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1	2	3	4	5	5	7
14	Gallocyan ine(C.I. Mordant Blue 10) methylest- er	t 1) $MOO_2 I_2$ pH =1.5 to 4.4 2) $MOO_3 pH=3$ to 5.3,0.4mM-Eth- anolic R(9ml), 10ml of aceta- tebuffer (pH = 2.5) 4ml of 1N -KCl	λmax = 630 to 640 nm	Many Metals interfere	Stability = 20 min.	19
15	3,4-Dihy- droxyazo- benzene.	pH = 1.3, 0.01M R in benzene	λmax = 550nm, 0.77 ppm € = 107,000		Shaking 5 min 1:2 complex, Reagent bl- ank is req- uired. Analysis of steel.	20
16	Gallein & hydrogen peroxide	1% poly(vinyl alcohol) (2ml) 3% H_2O_2 (1ml) methanolic 1mM -R(0.75ml) pH = 6.4 - 6.9 phosphate buffer.	λmax = 530nm, 1 to 20ppb S = 30pg/cm ²	Th, Cu, Ni,Cr(VI) Fe(III) interfere All ions except Cr(VI) masked with nit- rilotria- cetic acid.	Heating 90min at 60° water cooling 5 min. Rea- gent blank necessary 15 min wai- ting Analy- sis of was- te water.	21
17	Catechol Violet & Alizarin red(C.I. Mordant red)	1) pH = 2.7 2) pH = 3.8	1)λmax = 540nm, 1 to 50 μM 2)λmax = 480nm 0.5 to 5 ppm		 1:1 Complex 2:2 Complex Before ext- raction 10min boil- ing is nec- ssary. 	22

1	2	3	4	5	6	7
18	4-(2-thi- azolylazo catechol	I) 40% acetone pH = 3.2-3.8 II) pH = 5.4 to 6.2	$\lambda \max II = 530 nm$ 2 to 20 μM E = 54,000		I) 1:1 Complex II) 1:2 Complex	23
19	phenylfl- uorone	1 M HClO ₄ (3ml) 1_{m} M R in etha- nol 0.06M HCl (2ml) Ethanol (1ml)	λmax = 518 nm, 0.12 to 0.96 ppm	Zr and Nb		24
20	2',3,4'- Trhydroxy azobenze- ne-4-sul- phuric acid.	10 to 150 mM in HCl, H ₂ SO ₄ H ₃ PO ₄ or HNO ₃	λmax = 460 nm 0.2 to 3.8 ppm € = 18,500		1:2 Complex	25
21	4-Butyry- lpyrogal- lol (2', 3',4'-Tr- ihydroxy butyroph- enone)	<pre>1) pH = 5.2 to 6.5 2) With I in presence of hydroxyl amine pH = 4.2 - 5.2</pre>	 λmax = 355 nm is measured at 410nm, 0.4 to 16 ppm. λmax = 350 nm 0.4 to 40 ppm 	Prior ex- traction of Fe(III) is neces- sary.	1:2 Complex	26
22	4-Propio- nylpyroga- llol(2', 3',4'-Tr- ihydroxy propioph- enone)	pH = 2.5 to 6	λmax = 390 nm 0.2 to 12 ppm € = 8635	Fe(III), U(VI) and Cr(III)	Analysis of alloy Fe + Ni + Mn +Co 1:2 Complex	27
23	4-Galloyl pyrogall- ol	pH = 6.04	入max = 420 nm 1 to 20 ppm	_	_	28
24	Quinaliz- arin	pH = 5,5 fold excess R, 50% ethan- olic medium	λmax = 540 nm 1 to 10 ppm S = 0.0077µg/cm ²	Many foreign species interfere	1:1 Complex 30 min waiting	29

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1	2	3	4	5	б	7
25	N-benzoyl -N-phenyl hydroxyl- amine			_	Determinat- ion of Mo in rocks & minerals	30
26	Trioctyl or dinon- yl amine			_	Recovery of Mo from wa- ste water four step extraction is necessary	31
27	N-(4-nit- rocinnam- oyl)-N-(4 -chlorop- henyl) hydroxyl amine.					32
28	Tri-n-oc- tylamine	H ₂ SO ₄ media			The method is used for separation of fission product	33
29	2,7-Dihy- droxy fl- uorescien (DHF) and cetyltri- methyl ammonium bromide	0.1 to 0.8 M HCl	$\lambda \max = 520 \text{ nm},$ 0 to 6 µg/10ml $\varepsilon = 133,000$		Complex is 1:2 Mo is determined satisfacto- rily in al- loy, steels & minerals.	34
30	TBP and TOPO	Aq. HCl, HNO3 or H ₂ SO4				35

1	2	3	4	5	6	7
31	Malachite green and p-Chloro- mandelic acid	pH = 2 to 4	λmax = 630nm. 0.10 to 4.0 μg € = 106,000	-	Mo is dete- rmined in mild steels with satis- factory results.	36
32	Neotetra- zolium Chloride and thio- cyanate	HCl ascorbic acid media	$\lambda \max = 470 \text{ nm}$ 0.3 to 3.8 ppm $\varepsilon = 24,700$, 0.004 µg/cm $\delta = 2.78$	-	Mo in river water is determined Complex ex- tracts in presence of Tritonx-100	37
33	NN'-Diph- enylthio- carbomoh- ydroxamic acid.	0.4 to 0.5 M	λmax = 275 nm 0.5 - 10 μg/mL	Fe(III) & V(V) are masked with ascorbic acid and Cu with thiourea	1:3 Complex Mo present in steel is determened.	38
34	2-Salicy- lidenimi- nobenzoh- ydroxamic acid		-			39
35	(2-Pyrid- inyl met- hylene) amino-2- benzohyd- roxamic acid		λmax = 378 nm 0.2 - 3.0 μg/mL € = 27000		Satisfacto- ry determi- nation of Mo in alloy cast iron & pharmaceut- ical compo- und.	40

1	2	3	4	5	6	7
36	Thiophene -2-hydro- xamic acid(THA) & Adogen 464		λmax = 370 nm 0.2 - 3.8 μg/mL € = 23400		Determined Mo in steel	41
37	Tris(2,6- dimethoxy phenyl) Phosphine	6 M HCl				42
38	3,6-Dihy- droxypth- alimide bis thio- semicarb- azone.	pH = 2.6 Chloroacetate buffer 0.03% R in DMF	<pre></pre>			43
39	2,2'-Dih- ydroxy benzophe- none thi- osemicar- bazone	0.5M HCL(20ml) 0.2% ethanolic R (20ml), 2% SnCl_0.05ml	λmax = 500 nm 1.20 ppm	Dithiozo- ne is ne- eded for prior re- moval of interfer- ing ions	1:1 Complex waiting 8 min.	44
40	5-Octylo- xymethyl- 8-quinol- inol	3.0 mol/L HNO ₃	λmax = 380 nm € = 11400		Mo in NBS standard steel is determined satisfacto- rily.	45
41	5,7-Dibr- omo-8-hy- droxyqui- noline	pH = 2, 50µM Na ₂ MoO ₄ (10ml)	入max =360 nm		6 min waiting	46

	1	2	3	4	5	6	7
4:	2	5-Chloro- 8 hydroxy -7-idoqu- inoline	pH = 1 to 2, acetate HC1 buffer,2.5mM R in CHC1 (10m1)	λmax=392nm upto 6 ppm		1:2 complex Reagent bl- ank needed, 5 min shak- ing	47
4	3	5,7-Dibromo quinolin 8-01	4M-H ₂ SO ₄ , 0.7% of R in CHCl ₃	λmax=387nm € = 11,700	Fe(III), Nb, V(V), W(VI)& Si, Te masked with ascorbic acid	Mo present in stainle- ss steel is determined	48
4	4	 Benzoyl acetone 4-Benzoyl-3 methyl-1 phen- yl pyrozoline- 5-one 	1) pH = 2 to 3 0.015 M R in CHCl ₃ - butanol (1:1) 2) 3mM to 3M HClO ₄ or HCl	λmax=372nm 1 to 20 ppm € = 3900 λmax=414nm 10 - 200ppm € = 360			49
4!	5	3-Hydroxy-2- methyl 1-phen- yl-4-pyridone	pH=1to3.2,0.2M R in CHCl ₃ R in CHCl ₃ (10ml)	λmax=317nm 0.5 to 5ppm € = 25,000	V interf- ere prior extracti- on of V(VI) is necessary with same reagent	1:2 complex Reagent bl- ank needed	50
4	6	3,3',4,4',5- pentahydroxy- benzophenone	рН > 5.2	\lambda max=375nm e measured at 410 nm 0.2to 16ppm e = 15,800	At pH 4.6 Prior ex- traction ofFe(III) with AA + pyridine needed Al U or Ti(TY) & Cu(II) interfere		51

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1	2	3	4	5	6	7
47	4-Hydroxy-3-me rcapto coumar- in	2M HCl (5ml) 0.5% R (5ml)	\lambda max=560nm 1 to 7ppm € = 12,000 S=8.12ng/cm ²	_	1:2 complex	52
48	Dithizone quinolin 8-01	pH=3.2 57.8um R in TBP			_	53
49	2-Aminobenzene thiol	pH = 2, 2% R in CHCl ₃ (5ml)	λmax=700nm 0.5to4.5ppm	Bi(III), Sn(II) interfere for Ni,Fe prior ex- raction is needed	Stability 2 h 5 min shaking	54
50	Potassium propylxanthate	2M HCl, pH≌1.1 HCl glycine buffer 1% aq. R (1ml)	λmax=510nm 1 to 14ppm	_	1:2 complex at 20 [•]	55
51	Toluene-3,4- dithiol	6M HCl, Anhyd. acetic acid (25ml) H ₃ PO ₄ (2ml) R(in 100 ml of 10% NaOH 5ml)+1gm of me rcapto acetic acid	λmax=705nm 25 to 100μg	_	Waiting 3hr 5min shaking	56
52	K-Ethylxantha- te	10M-HCl,aq.1% K.ethylxantha- te (2ml), aq.5% NH ₄ SCN (2ml)	λmax=380 or 470 nm		Multiple extraction Reagent blank is needed, 2min shaking	57

1	2	3	4	5	6	7
53	Sodium diethyl dithiocarbama- te	11N-HCl (11ml) 10ml CHCl ₃ ,5% R (5ml)	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	Serious interfere nce of V(v Cu(II) Ni Cr(VI) & Ag		58
54	1,5-Diphenyl carbazone			_		59
55	Salicyloldehy- de isonicotin- oyl hydrazone (SAIH)	1N HClQ4 EDTA ascorbic acid	λmax=430nm 0.4to12 ppm € = 6500			60
56	1-Nitroso-2- naphthol	2-3M-HCl, 0.5 mM R	λmax=380nm 2 to 20ppm € = 2500		1:1 complex Toremoue reagent ex- tract is scrbed with NaOH. Anal- ysis of steel	61
57	2-Hydroxy-1- naphtaldoxime	pH = 3 acetate buffer	入max=400nm upto53.7ppm E= 1750	Oxalate interfere Fe(III) interfer- ence mas- ked by KI	1:1:1 Complex	62
58	Resacetopheno- ne oxime	0.1M Solution in aq. 50% ethanol 4mM HCl	λmax=400nm upto 230ppm	Oxalate tartrate, citrate, acetate, EDTA, Bo- rate, PO and Al interfere		63

1	2	3	4	5	6	7
59	Benzoin⊷∢- Oxime	NaCl(sat)+HCl Mo determined by thiocyanate method	入max=490nm		Waiting 1hr shaking necessary	64
60	2-Hydroxy-5- Methoxy benza- ldoxime	pH=3.2 to 3.8	λmax=370nm 5 to 70ppm λmax=400nm 5 to 110ppm	_	1:1 Complex Analysis of oil	65
61	Resacetopheno- ne oxime	0.1M-HCl 20%by vol. of cyclo- hexanol, 10 fol d excess R	λ max=400nm 0.1-0.5mg/m] $\epsilon = 100$ S=0.96mg/cm		1:2:1 Complex (Mo:Oxime: Cyclohexan- ol)	66
62	Imidoyl phenyl hydrazine	10M-HCl(12ml)+ NH ₄ SCN 20%(3ml) +ascorbic acid 20% (2.5ml)	λmax=460nm upto 3 ppm e = 17300	Fe(III) & Nb(V) masked with oxalate	1:2:1 Complex Mo determined present in ore and alloys	67
63	Bromopyrogall- ol(I) and Hexadecyltri methyl ammoni- um(II)	pH=1(HCl), 4- fold molar ex- cess of I and 20-fold molar excess of II	λmax=630nm 0.02 to 1.2 µg/ml € = 84,000	Ti,Cr(VI) Mn(III) interfere V masked with ascorbic acid	1:2:2 Complex	68
64	Salicylfluoro- ne + cetrimide	0.2 to 0.8MHC1	λmax=530nm upto0.32ppm € = 140000	Serious interfer- ence of W and Ti	Analysis of alloy steel 1:2:2	69
65	Promethazine hydrochloride	2.5M-H2SO4 (2.5ml) + 5N- KSCN(2.5ml) Aq 10% ascorbic acid(2ml)0.02N -R 5ml	λmax=465nm 5 to 50 µg	Co(II) & Cu(II) interfere	R is added after 15min	70

	1	2	3	4	5	6	7
	66	Benzohydroxam- ic acid	pH=0.5 to 2.2	λmax=370nm 0.4to 40ppm € = 2200	SnCl ₂ & F &ascorbic acid used for mask- ing other constitu- ents of the samp- les		71
	67	Thiocyanates & amidopyridines	1.5 to 7M HCl or 1.2 to 6M H ₂ SO _{4,} SCN+amido pyridine	λmax=470nm 0.5 to 4ppm € = 15000 to 19000			72
	68	N-N'-Diarylbe- nzamidines in presence of thiocyanate	0.57M ascorbic acid(5ml)2.63M NH ₄ SCN(3ml), made 4M in HCl, 25ml R in benzene	∖max=465nm			73
	69	4-Methoxy-N-p- tolyleinnamo- hydroxamicacid	6M-HC1,0.01M-R in CHCl ₃ (5ml)	λmax=390nm 0.05to 1ppm € = 110000	_	Shaking 2 to 5 min.	74
and the second se	70	Lobeline + SCN		入max=465nm 0.13to4ppm	Cu,Ti(IV) Co and W must be separated		75
	71	Heamatoxylin and cetrimide	 in absence- of ascorbic acid in presence of ascorbic acid pH = 5.6 - 6.8 	入max=610nm 入max=415nm 3 to 11ppm		Used for analysing steel	76

1	2	3	4	5	6	7
72	N,N'-Diphenyl- p-toluamidine hydrochloride + SCN	2 to 5M HCl 0.05 to 1 ascorbic acid 0.05 to 0.8M SCN, 30-200 fold R	λmax=470nm 0.4 to 5ppm		Stability 40 hrs.	77
73	Hydroxyamidine + SCN	3.5 M HCl10% ascorbic acid (5ml) 5%KSCN (5ml) 0.1%R in benzene(5ml)	\\max=470nm Analytical range = 5to18 ppm		1:2:2 Complex 2 min Shaking re- agent blank necessary	78
74	TritonX-100 & thiocyanate	0.22M-H ₂ SO ₄ 0.8% R, 0.32M ascorbic acid, 0.3M-SCN	λmax=468nm upto 4.6ppm € = 17200		Presence of iron neces- sary, 10min waiting, Analysis of steel	79
75	Bromopyrogall- olred(I) + Hexadecyl pyridinium chloride(II)	1) 0.05 to 5M H ₂ SO ₄ i.e 40µM in I+ 2) 0.2mM in II	λmax=630nm, 0.08-1.4ppm at pH = 1 € = 80000	W(VI) interfere Fe(III) masked with ascorbic acid	1:2:2 Complex Analysis of steel soya- bean, wheat etc.	80
76	Pyrogallcl red + Benzyl dime- thyl anilinium chloride	pH = 4	λmax=582nm, 0.7 to 6ppm, € = 21300	annan ann an Anna ann an An	1:2:2 Complex	81

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1	2	3	4	5	6	7
77	Thiocynate and nitron	3-4M-HCl,10% FeSO ₄ (1ml),10% ascorbic acid (10ml), 10% KSCN, (2ml) 0.5g/L nitrogen sulphate(10ml)	入max=465nm 1.2to12 ppm	Mn(VII), Ti(IV) & peroxide interfere	Reagent blank is necessary, 20 to 40min wait ing shaking 1min.	82
78	Pyrogallol red II and Hexade- cylpyridinium chloride(I)	pH=4.7,acetate buffer 10mM-I, 1mM-II (1.5ml) in methanol	λmax=610nm upto 3 ppm S=0.0028 µg/cm ²	For Al, Te(III) & Tb(IV) masking is needed	Waiting 50 min. Reagent blank needed.	83

EXPERIMENTAL

Standard Molybdenum Solution :-

A standard solution of molybdeum was prepared by dissolving 0.46gm of ammonium heptamolybdate in about 100ml of distilled water. The solution was heated gently on hot plate to obtain a clear faint bluish solution. The solution was diluted to 250ml in a volumetric flask with distilled water. The molybdenum content of the solution was determined gravimetrically by the 8-hydroxy quinoline method. For standardisation of molybdenum, an aliquot of the solution was neutralised to methyl red and then acidified with few drops of sulphuric acid. addition of 5ml of 2N sodium acetate and 60ml After of distilled water, the solution was heated to boiling. Molybdenum was precipitated by the addition of 38 solution of oxine in dilute acetic acid until the liquid became perceptibly supernant yellow. The precipitate was digested by gentle boiling and simultaneous stirring for 3 minutes. The precipitate was filtered through a sintered glass crucible and washed with hot water until free from the reagent. The precipitate was dried to a constant weight at 130-140°C a oven. It was finally weighed as $MoO_2(C_9H_6ON)_2$. in Suitable concentration containing 250 µg/ml was prepared as needed by diluting the stock solution with distilled water.

Reagent Solution :-

A 0.2% (w/v) solution of the reagent was obtained by dissolving 0.2gm of the reagent 3,5-dichloro SAT in 100ml of hot ethyl alcohol. The solution is quite stable towards light and heat. The reagent solution can be kept over a week period.

Stannous Chloride Solution :-

4gm of colourless stannous chloride was dissolved in boiling 20ml concentrated HCl. A clear solution was then diluted to 100ml with distilled water. This gives 4%(w/v) solution of stannous chloride. This solution was prepared daily.

All solutions of diverse ions were prepared by dissolving AR grade chemicals in distilled water or dilute hydrochloric acid. The acids used to adjust the acidity of the medium were also of AR grade.

Apparatus :-

All absorption measurements were made with the Carl-Zeiss (JENA) spectrophotometer using 1cm quartz cells.

Recommended Procedure :-

To an aliquot of the solution containing upto 250µg of molybdenum, 5ml of 0.2% reagent solution in ethanol was added. The mixture was adjusted to 3N acidity with respect to H_2SO_4 by addition of 9N H_2SO_4 followed by 1ml stannous chloride solution. The flask was briskly shaken and was made to 25ml with distilled water. The absorbance of the pink colour complex of molybdenum was measured at 525nm against water as a blank.

RESULTS AND DISCUSSION

Spectral Characteristics :-

The absorbance spectrum of the Mo -3,5-dichloro SAT complex using 10 ppm of molybdenum and 0.2% reagent against the water as a blank is shown in Fig.1. The solution of 3,5-dichloro SAT in ethanol is colourless and does not absorb significantly in the visible region. The absorption measurements were made in the region 400-600 nm against the water as a blank. The complex of Mo(VI) with the reagent 3,5-dichloro SAT exhibits absorption maximum at 525nm. The complex of Mo with chloro compounds of SAT is more stable than the SAT. The complex is not extracted by benzene, nitrobenzene, chloroform or carbon tetrachloride. With MIBK and amyl alcohol the pink colour changes to yellow green. Benzyl alcohol extracts the complex but the solution is very unstable. The molar extinction coefficient as determined from Beer's law plot is $6.469 \times 10^3 L \text{ mole}^{-1} \text{ cm}^{-1}$. The Sandell sensitivity of the reagent was 0.015 at 525nm.



Effect of Acidity :-

In order to obtain the optimum concentration range for the full colour development of molybdenum complex, the sulphuric acid concentration was varied from 0.5 to 7.0 N with 10ppm of molybdenum and 0.2% reagent in ethanol. It was found from the curve of absorbance versus H_2SO_4 normality that the optimum concentration range of sulphuric acid for the full colour development of the molybdenum complex is 2.5-7N H_2SO_4 (Fig.2). If the sulphuric acid concentration is lower than 0.5N a precipitate is formed. There is no significant effect of acidity on the absorbance of the molybdenum complex at greater than 2.5N acidity. Hence, 3.0N sulphuric acid media was recommended for all the subsequent absorbance measurements.

Effect of Stannous Chloride Solution :-

In order to find out the optimum volume of 4% solution, the volume of stannous chloride solution was varied from 0.25 - 3.0ml. From Fig. 3 it was observed that the optimum volume range of 4% stannous chloride solution for the full colour development of molybdenum complex is 2.0-3.0ml. At less than 0.75ml stannous chloride solution, precipitation occurs, whereas the excess of stannous chloride solution is immaterial. Hence for all the subsequent spectrophotometric measurements 2.5ml of 4% stannous chloride solution was



used.

Order of Addition of Reagent :-

In procedure the order of reagents is also important. It is necessary to add the reagent before the stannous chloride solution. If the reagent is added after the stannous chloride solution, the pink colour complex is not formed. Sulphuric acid can be added either first or last.

Effect of Reagent Concentration :-

Solutions containing the same amount of molybdenum (10ppm) but different amounts of the reagent varying from 0.25-5.0ml of 0.2% alcoholic reagent were prepared. The colour was developed as outlined in the recommended procedure and the absorbance of the complex was measured at 525nm against water as the blank. The results of studies are shown in Fig.4 which indicate that 10ppm of molybdenum required a 2ml of 0.2% reagent solutions (2ml 0.2% reagent + 3ml of alcohol). At high reagent concentration turbidity was formed the and the absorbance could not be measured. Thus 2ml of the reagent was used for all subsequent measurements which corresponds to 6 fold molar excess of the reagent relative to Mo(VI).

Effect of Alcohol :-

In order to find out the amount of alcohol needed A11715



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during the complexation of Mo(VI)-3,5-dichloro SAT complex, the amount of alcohol was varied between 0.5-11.5ml. It was found from the curve that the amount of alcohol required for full colour development of Mo complex is in the range 1.5-3.0ml(Fig.5). At less than 1ml alcohol, precipitation occurs whereas decrease in absorbance occured at greater than 5ml alcohol. Hence for all the subsequent measurements 3ml alcohol was recommended.

Validity of Beer's Law :-

The solution containing different amounts of molybdenum in the range 50 to 500 μ g were used for the study of the validity of Beer's Law. The colour was developed as per the recommended procedure using 7.6 x 10⁻³ M reagent and the absorbance was measured at 525nm against the water as a blank. The curve in Fig.6 shows that Beer's law is valid in the range 2 to 20 ppm of molybdenum. However, the optimal concentration range was found to be between 4-12ppm Mo.

Composition of the Complex :-

In order to establish the composition of the complex, the equimolar solutions of metal and ligand 1.7×10^{-3} were used. The Job's method and mole ratio method were used for determining the composition of the complex. A series of solutions were prepared in which mole fraction of reagent was varied from 0.1-0.9.



Acidity of the solutions was adjusted to 3N with 9N H₂SO₄ and the colour of the complex was developed as per the recommended procedure and the absorbances of the solutions were measured at 525nm against water as a blank. The plot of the absorbance versus the mole fraction of the ligand indicates that the molybdenum(VI) forms 1:3 complex with the ligand 3,5-dichloro SAT (Fig.7).

The composition of the complex was verified by mole ratio method. For this method the equimolar solutions of metal and ligand were used (3.4×10^{-3}) . A of solutions containing fixed volume of series molybdenum and different amounts of the reagent were prepared. The 3N acidity was maintained by adding sulphuric acid and the colour of the complex was developed as per the recommended procedure. The absorbance of solutions were measured at 525nm against water as a blank. The plot of the absorbance versus the reagent to metal ratio(Fig.8) confirms the results obtained by the application of Job's method.

Effect of Diverse Ions :-

The effects of large number of diverse ions on the determination of 0.25mg of Mo(VI) using 7.6 x 10^{-3} M reagent was studied. The solutions were prepared containing fixed amount of molybdenum and various amounts of foreign ion. The colour of the complex was



developed by following the recommended procedure and the absorbance was measured at 525nm against water as a blank. An error of less than 2% in absorbance was considered to be tolerable.

Table No. 2 shows the tolerance The limits obtained for various foreign ions. Initially, the large excess of foreign ion was added to the molybdenum (20 fold excess for cations). When solution the interference was intensive, the tests were repeated with successively smaller amounts of foreign ion. The results in Table No. 2 shows that the cations such as V(V), Ga(III), Sb(III), As(III), Al(III), In(III) and Ru did not interfere when present in 20 fold excess relative to molybdenum. The tolerance limit found for cations like Ti(IV), Mg(II), Mn(II), Fe(III), KI is 4mg. The ions which interfere in the determination of molybdenum include : Pb(II), Hg(II), Tl(III), Zr(IV), Zn(II), Cd(II), Re(VI), Os(VIII), Au(III), Ce(IV), Se(IV), Cr(VI).

Reproducibility, Accuracy and Sensitivity Data :-

To study the reproducibility and accuracy of the method, ten different identical solutions containing 7.5ppm molybdenum were performed as outlined in the procedure. The absorbance of each solution was measured at 525nm against water as a blank. The concentration was determined using the calibration curve. The results are

Mo(VI) = 10 ppm;	Aqueous phase = 3N H2SO4
3,5-dichloro SAT = 0.2%	in alcohol; $\lambda \max = 525 nm$.
FOREIGN ION	TOLERANCE LIMIT in mg
 V (V)	5
Ga(III)	5
Sb(III)	5
Mn(II)	4
Bi(III)	4.5
Pb(II)	Interfere
Hg(II)	Interfere
T1(III)	Interfere
Zr(IV)	Interfere
Zn(II)	Interfere
As(III)	5
Mg(II)	4
Ni (II)	3
Al (III)	5
Cd (11)	Interfere
Re(VI)	Interfere
Os (VIII)	Interfere
Au(III)	Interfere
T1(IV)	4
U(VI)	3
K1	4
Fe(111)	4
In (III)	5
$\operatorname{Ir}(V1)$	
Se(IV)	
Cr(V1)	Interiere
	2
Te(IV)	V.5

TABLE NO. 2 :- EFFECT OF DIVERSE IONS.

shown in Table No. 3. It is observed that there is an excellent agreement in the experimental values. The method has high precision and accuracy.

Average of these ten readings are calculated. Deviations from these average readings was found out at each case and then standard deviation was calculated. By using standard deviation, the reproducibility of the results with 95% confidence limit was calculated. The Sandell sensitivity of the reagent as calculated from Beer's plot was found out to be $15ng/cm^2$. From the mole ratio plot⁸⁴, the stability constant K of the complex was calculated. The value of K is 6.945 x 10^{-16} . TABLE NO. 3 :- PRECISION AND ACCURACY OF THE METHOD.

Sr. No.	Absorbance observed	ppm of Mo found,(x)	x - x	$(x - \overline{x})^2$
1	0.510	7.5	0.01	0.0001
2	0.505	7.4	0.09	0.0081
3	0.510	7.5	0.01	0.0001
4	0.515	7.6	0.11	0.0121
5	0.505	7.4	0.09	0.0081
6	0.510	7.5	0.01	0.0001
7	0.515	7.6	0.11	0.0121
8	0.510	7.5	0.01	0.0001
9	0.515	7.6	0.11	0.0121
10	0.510	7.5	0.01	0.0001
TOTAL		75.1		0.0530

Amount of Mo = 7.5 ppm.

Average value $(\overline{x}) = \frac{75.1}{10}$

Standard deviation (d)

$$d = \sqrt{\frac{(x_1 - \overline{x})^2 + (x_2 - \overline{x})^2 \dots (x_n - \overline{x})^2}{(n-1)}}$$

$$= \sqrt{\frac{0.053}{9}}$$

$$= 0.08$$

Reproducibility with 95% confidence limit

$$= \bar{x} \stackrel{t}{=} 2.26 \times \frac{d}{\sqrt{n}}$$

$$= 7.51 \pm 2.26 \times \frac{0.08}{\sqrt{10}}$$

$$= 7.51 \pm 2.26 \times \frac{0.08}{\sqrt{10}}$$

$$= 7.51 \pm 2.26 \times \frac{0.08}{3.16}$$

$$= 7.51 \pm 0.057$$
Error (E)
$$= 0bserved reading - Actual reading$$

$$= 7.51 - 7.5$$

$$= 0.01$$
Relative error
$$= \frac{0.01 \times 100}{7.5}$$

$$= 0.13$$

% coefficient of variation

c.v. =
$$\frac{\int x 100}{\overline{x}}$$

where $\oint -$ standard deviation.
= $\frac{0.08 \times 100}{7.51}$
= 1.0

Molar Extinction coefficient Absorbance $\varepsilon = ----- x = 1000 x Atomic Weight$ ppm

= slope x 1000 x Atomic Weight

Sandell's Sensitivity (S) $S = 10^{3} \times \text{Atomic Weight x Cmin}$ where Cmin = $\frac{\text{Dmin}}{\text{€ x b}}$ $= 10^{3} \times 96 \times \frac{0.001}{6.432 \times 10^{3} \times 1}$ $= 0.015 \text{ µg/cm}^{2}$ $= 15 \text{ ng/cm}^{2}$

Stability constant K

$$K = \frac{\prec C (n \prec C)^{3}}{C(1 - \prec)}$$

$$= \frac{0.12 \times 4.78 \times 10^{-5} (3 \times 0.12 \times 4.78 \times 10^{-5})^{3}}{4.78 \times 10^{-5} (1 - 0.12)}$$

$$= \frac{2.924}{4.21} \times 10^{-15}$$

$$= 0.6945 \times 10^{-15}$$

$$= 6.945 \times 10^{-16}$$

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