Chapter-III

Photometric Determination of Molybdenum (V) with 5-Methyl Salicylaldehyde Thiosemicarbazone

CHAPTER III

PHOTOMETRIC DETERMINATION OF MOLYBDENUM (V) WITH 5-METHYL SALICYLALDEHYDE THIOSEMICARBAZONE

INTRODUCTION

Molybdenum is gray, heavy, hard and refractory metal which is useful principally in the targets of x-ray 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 non-ferrous 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.

Its most stable oxidation states are +3, +5 and +6, the last being the commonest. As a trace element it is essential to the health of plants 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 photometric determination of molybdenum (VI) in the literature. A critical review has been given by Busev (1) and by Khosala et al.(2). Despite of several disadvantages the classical thiocynate method is frequently used as one of the most accurate spectrophotometric methods for the determination of molybdenum (3-5). Improvements of thiocynate method have also been reported in the literature (14,17). Photometric methods for determination of molybdenum based on the formation of ternary complex of molybdenum thiocynate with the organic base are well known (7,13,16,21,35,39,41,43, 51,56,60,100,101,102,104). The reported methods are highly sensitive and rapid but suffer from interference of many metal ions.

Among the various dyes proposed for determination of molybdenum colourimetrically, the most recent are some monoazo-derivatives of pyrogallol (9),2-thiopyrogallol (23), 5-Br-PADP(30), gallocyanine (31), 3,4-dihydroxyazo-benzene (42), gallein (44), catechol violet (45), 4-(2-thiazolylazo) catechol(57),phenyl-fluorone (59), 2',3'4'-trihydroxyazobenzene-4-sulphuric acid (63), 4-butyryl pyrogallol (73), 4-propionylpyrogallol (75),4-galloyl-pyrogallol (108),quinalizarin (112).

Formation of mixed ligand complexes increases the selectivity and sensitivity of the determination along with the

enhancement in the solubility in organic solvent and the extraction rate. Procedures have been developed for photometric determination of Mo(V) based on the formation of mixed complex by association of a co-ordinately saturated charged complex with a ligand counter ion. Acid dye has several functional groups,in particular sulphonic acid groups which do not take part in chelate formation. Here charged chelates are formed. For neutralisation of such compounds, the use of strongly basic organic cation quarternary ammonium salts (11,12,25,37,40,50,67,68), Zephireamine (96,106) and other bases (38,46,87,99,105,115) is effective. Numerous chelating agents are reported as sensitive reagents for determination of molybdenum (V). These include hydroxamic acids (8,15,24,32,62,66,77,94,103), tiron (4),2,4-dihydroxy-3-mercapto benzoic acid (18), derivatives of thiosemicarbazone (6,19,58), quinoline and its derivatives (22,76,92),ketones (26,72,93), coumarines (27), thioligands (34,79,82,91,110),1-nitroso-2-napthol (52) oximes (33,64,69,81).

However, the spectrophotometric methods based on these reagents suffer from various difficulties including low selectivity, tedious operation and interference from ions commonly associated with molybdenum such as Cu,Co, Ni,Fe(III),Bi,Ti(IV),Zr(IV),Nb(V), V(V) and W(VI). Hence these methods are unsuitable for routine use.

The reagent proposed here reacts with Mo(VI) to form the red complex with the sharp maximum absorption at 510 nm when the alcoholic reaction mixture 3M in HCl is heated on water bath

for 20 minutes. The present method has the certain advantages over the earlier one (6). It does not require the addition of separate reducing agent like stannous chloride, ascorbic acid or thiourea and also the presence of Cu(II) ion or Fe(III) ion to prevent over reduction of molybdenum. The method is simple and sensitive.

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

Experimental

Standard Molybdenum Solution :

A standard solution of molybdenum was prepared by dissolving 0.45 gm of ammonium molybdate in about 100 ml 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 volumetric flask with distilled water. The molybdenum content of the solution was determined gravimetrically by the 8-hydroxy qunoline method. For standardisation of molybdenum, an aliquot of the solution was neutralised to methyl red and then acidified with few drops of sulphuric acid. After addition of 5 ml of 2N sodium acetate and 60 ml of distilled water, the solution was heated to boiling. Molybdenum was precipitated by the addition of 3 % solution of oxine in dilute acetic acid until the supernant liquid became perceptibly yellow. The precipitate was digested

Table No.1 : Summary of the Reagents Reported for Mo(VI)

S.No.	Reagent	Medium	Conditions	λmax, molar extinction coefficient Beer's range and sensitivity	Interferences	Remarks	Ref No
1	2	3	4	5	6	7	8
1	Imidoyl phenyl-hydrazine	Benzene	10M-HCl(12 ml)+ NH_4SCN 20% (3ml) +ascorbic acid 20%(2.5 ml)	λmax =46 nm ∈ =17,300 upto 3 ppm	Fe^{III} & Nb^{V} are masked with oxalate	1:2:1 complex Mo determined in ore & alloys	7
2	N-Phenylbenzohydroxamic acid	$CHCl_3$	2M-HCl,+Aq.0.1% $FeSO_4$(2ml) +Aq. 0.1% NaF+ 0.1% R in $CHCl_3$(10ml)	λmax=395 nm, ∈ =3200 0.9 to 45 ppm	-	Shaking 15 min	8
3	4-(4-Idophenylazo) pyrogallol(I)and 4-(2,3,4-Trihydroxyphenylazo)-benzensulphonic acid(II)	-	1)For Mo^{VI}-I - 5 to 70m M H_2SO_4, 3 to 4 fold molar excess of R(I)	λmax =480 nm, ∈ =37,500 500; 0.06 to 3.4 ppm	-	1.2 complex	9
			2)For Mo^{VI} R.II- 5to 100 mM- H_2SO_4	λmax =460 nm ∈= 20,500 500 0.16 to 3.8ppm		1.2 complex	
4	Tiron	Xylene	0.02M-malonic acid, 0.08M Amberlite LA-2 in xylene at pH =3.0 Re-extracted into 0.25 M -NH_3	λmax =390 nm	-	Satisfactory for separation of Mo from multicomponent mixtures, Applied in the determination of Mo in steel & soil	10

Contd..

1	2	3	4	5	6	7	8
5	Bromopyrogallol(I) and Hexadecyltri methyl ammonium(II)	Aqueous	pH=1(HCl),4-fold molar excess of I and 20-fold molar excess of II	λ max =630nm , ϵ =84,000 0.02 to 1.2 $\mu g\ ml^{-1}$	Ti, Cr^{VI}, Mn^{III} interfere and V can be masked with ascorbic acid	1:2:2 complex C.V. $=<4.1\%$ of $\backsim 0.2\%$ of M_o	11
6	Salicylfluorone + Cetrimide	Aqueous	0.2 to 0.8 M HCl	λ =max =530nm, ϵ =140,000 upto 0.32ppm	W and Ti interfere seriously	1:2:2 complex Analysis of Alloy steel	12
7	Promethazine hydrochloride	$CHCl_3$	2.5M-H_2SO_4 (2.5ml)+5N-KSCN (2.5ml)Aq.10% ascorbic acid (2ml) 0.02N-R (5ml)	λ max =465 nm 5 to 50 μg	Co^{II} and Cu^{II} interfere	R is added after 15 min C.V.=0.3 to 1.5% Relative error = $\pm$1.5%	13
8	Thiocynate	Ethyl-methyl ketone	Conc.HCl(5ml), Aq.ascorbic acid	λ max=465 nm upto 6 $\mu g\ ml^{-1}$	-	Waiting 7 to 10 min shaking 30s,Reagent blank needed	14
9	Benzohydraxamic acid	Hexanol	pH =0.5 to 2.2	λ max=370 nm, ϵ=2200,0.4 to 40 ppm.	$SnCl_2$ & F^- and ascorbic acid are used for masking other constituents of the samples	-	15
10	Thiocynates and amido pyridines	Benzene	1.5 to 7M-HCl or 1.2 to 6M-H_2SO_4,SCN+amido pyridine	λ max=470nm ϵ =15,000 to 19,000 0.5 to 4 ppm	Limit for $\leq$2% interference $\backsim$0.4 mg ml^-	C.V.for 2 ppm. = 0.08%	16

Contd.

1	2	3	4	5	6	7	8
11	Thiocynate	$CHCl_3$	10M-HCl(1.2ml), $(NH_4)_2SO_4$ $FeSO_4 \cdot 6H_2O$ (1ml)in 0.1M-H_2SO_4,Aq.20% NH_4SCN(1ml) 20% $SnCl_2$(1ml)ethanol (10ml)+ H_2O	λmax =465 nm upto 4 ppm S =14ng Cm^{-2}	Oxalate and Re^{VII} interfere	Shaking 1 min Blank extract needed	17
12	2,4-Dihydroxy 3-mercapto-benzoic acid	Isoamyl alcohol	6M-HCl(5ml), 0.5% R (5ml)	λmax=490nm, ϵ =19,400 0.25 to 8ppm S=4.92 ng Cm^{-2}	W^{VI}, Re^{VII}, Fe^{III},and Pd^{II} interfere.Fe is masked with F^-	Analysis of high speed steel	18
13	3,6-Dihydroxypth alimide bisthi-osemicar bazone	Isopen-tyl alcohol	pH=2.6 chloroace-tate buffer, 0.03% R in DMF	λmax=425 nm in aqueous λmax=(dried extract)=435nm S=11 or 10 ng Cm^{-2} respectively	-	-	19
14	Flavon -3-ol-2'-sulphonic acid	Aqueous	R(Na salt)and $HClO_4$	λmax =370 nm, ϵ =14,000 0.69 to 8.20ppm	-	1:1 chelate,stabili-ty constant of the chelate =3.4 &I=1.0	20
15	N-N'-Diaryl benzamidines in presence of thiocynate	Benzene	0.57M ascorbic acid (5ml),2.63M NH_4SCN(3ml),made 4M in HCl extd. for 2 min with 25ml R in benzene	λmax=465 nm	-	-	21
16	5,7-Dibromoquinolin 8-ol	$CHCl_3$	4M-H_2SO_4,0.7% soln.of R in $CHCL_3$	λmax=387nm, ϵ =11,700	Fe^{III},Nb,V^v,W^{vl} and Si,Te is masked with ascorbic acid	Method is suitable for determination Mo^{vl} in stainless steel.	22

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1	2	3	4	5	6	7	8
17	2-Thiopy-rogallol	Isoamyl alcohol	1.2M-HCl,0.5% aq.R (5 ml)	λ max=525nm, ϵ =19,000 0.25to 10ppm	W^{Vl} and pd^{II} interfere	Stability= 2h Analysis of steel	23
18	4-Methoxy-N P-tolylcinn-amohydroxa-mic acid	$CHCl_3$	6M-HCl,0.01M-R in $CHCl_3$(5ml)	λ max=390nm, ϵ=1.1×10^5 0.05 to 1 ppm.	-	Reduction of V(V) and fluoridemaking of Ti needed.shaking 2 to 5 min.	24
19	Pyrogallol red & Hexa-decyltrimet-hyl ammonium bromide (Cetrimide)	Aqueous	pH=4 acetate buffer 0.015% R in aq.ethanol 1% Cetrimide	λ max=570 nm ϵ = 53,000	Ti inter-fers	1:2:2 complex Reagent blank needed	25
20	1)Benzoyl acetone	$CHCl_3$: Butanol (1:1)	1)pH=2 to3,0.015 M R in $CHCl_3$-butanol(1:1)	λmax =372 nm,ϵ=3900 1to 20 ppm	-	C.V.= <10%	26
	2)4-Benzoyl 3-methyl 1-phenyl pyrazoline -5-one	$CHCl_3$-Butanol 3:2	2)3mM to 3M $HClO_4$ or HCl	λmax=414 nm, ϵ = 360 10 to 200 ppm	-		
21	4-Hydroxy-3-mer capto-coumarin	Chloroform	2M-HCl(5ml) 0.5% R(5ml)	λ max=560nm ϵ =12,000 1 to 7 ppm,S=8.12ng Cm^{-2}	Cu^{II},V^{V} and W^{Vl}(30 ppm could be tolerated)	1:2 complex C.V.=2.7%	27
22	Thioglycolic Acid+N-Benzylaniline	Chloroform	0.5M-HCl,1m Thioglycolic acid(2ml), shaken with 5 of 5% N-Benzylaniline soln.in $CHCl_3$	λ max=355 to 360nm ϵ =3050 ,5 to20ppm	Cr interfered seriousl y	Shaking 1 to 2 min, stability = 2.5 h	28

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1	2	3	4	5	6	7	8
23	Hydrogen Peroxide	-	1.4M-H_2SO_4,36mM H_2O_2 and 2.28M-H_3PO_4	λ max=350nm	Fe^{III} is masked with H_3PO_4	750fold U(VI)is tolerated.Sensitivity of method is 0.03% maximum error =5%	29
24	NH_2OH-5-Br-PADP(2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol,I)+Poly(ethanediol octylphenyl ether)	Aqueous	-	λmax=600 to 605nm ϵ =48,000 upto 3 ppm	Be, Mg,Ca,Sr, Ba,U^{VI},Mn^{II}, Fe^{III},Co and Ni need masking	1:1:1 complex	30
25	Gallocyanine (C.I.Mordant Blue 10)methylester	Aqueous	1)MoO_2I_2-pH=1.5 to4.4 2)MoO_3-pH=3 to 5.3 0.4mM-Ethandic R(gml), 10ml of acetate buffer soln.(pH=2.5),4ml of 1N-KCl	λmax=630 to 640	Many metals interfere	Stability 20 min	31
26	2-Methoxy-N-P-tolylbenzohydroxamic acid	Isoamyl alcohol	pH=.25 to 3.5	λmax=355 nm 0.3 to 11 ppm	-	Std.deviation=0.01 to 0.02 for 6 to 100 ppm.	32
27	2-Hydroxy-1-napthaldoxime	Aqueous	pH=3 acetate buffer	λmax=40nm, ϵ =1750 upto 53.7 ppm	Oxalate interferes,interference by Fe^{III} is masked by addition of KI	1:1:1 complex	33
28	Dithizone	TBP	pH=3.2,57.8 µm-R in TBP	-	-	-	34
29	Lobeline+SCN	$CHCl_3$	-	λmax=465nm, 0.13 to 4ppm	Cu^{II} Ti^{IV},Co^{II} & W^{VI} must be separated	-	35
30	β-recorcylic(2,4-dihydroxybenzoic acid	Aqueous	pH=3.5 to 4.5	λmax=350nm	-	1:1 complex	36

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1	2	3	4	5	6	7	8
31.	Heamatoxylin and Cetrimide	Aqueous	1)in absence of ascorbic acid 2)in presence of ascorbic acid -pH=5.6 to 6.8	λmax=610 nm λmax=415 nm 3 to 11 ppm	-	Method is recommended for use in analysing steel	37
32	Pyrogallol red+Benzyl dimethyl anilinium chloride	Butanol	pH = 4	λmax=582nm, ϵ=21,300 0.7to 6ppm	-	1:2:2 complex	38
33	N N'-Diphenyl -P-toluamidine hydrochloride +SCN	Benzene	2to5M-HCl,0.05 tol ascorbic acid, 0.05 to 0.8M SCN^-, extd for 1 min 30-200 fold R	λmax=470 nm 0.4 to 5 ppm	-	Stability 40 h	39
34	Pyrogallol red and Hexadecyl-trimethyl ammonium ion	Aqueous	pH =3.6,20 mg of ascorbic acid, acetate-EDTA buffer soln.Ethanolic R+ Amine	λmax=600 nm, =90,000 0.1 to 0.4ppm	Tungstate,I^- tartrate, citrate and oxalate interfere W & V need prior separation	1:2:4 complex,waiting 10 min.Reagent blank needed std.deviation = 11ng for 10 µg. Relative error = ± 2.5%	40
35	Hydroxyamidine +SCN	Benzene	3.5M-HCl,5ml of each of aq.10% ascorbic acid,5%,KSCN,0.1% R in benzene	λmax=470 nm Analytical range = 5 to 18 ppm	-	1:2:2 complex,shaking 3 min.Reagent blank needed C.V.=0.98%	41
36	3,4-Dihydroxy azo-benzene	Benzene	pH=1.3,0.01 M R in benzene	λmax=550 nm, $\epsilon \simeq$ 107,000, 0.77 ppm	-	1:2 complex,Reagent blank needed shaking 5 min Analysis of steel	42
37	Triton X-100 and thiocynate	Aqueous	0.22M-H_2SO_4,0.8%R, 0.32M-ascorbic acid, 0.3M-SCN^-	λmax=468nm, ϵ=17,200 upto 4.6ppm	-	Waiting 10 min.Presence of iron necessary. Analysis of steel	43

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1	2	3	4	5	6	7	8
38	Gallein and hydrogen peroxide	Aqueous	1% poly(Vinyl alcohol) (2ml),3% H_2O_2(1 ml) methanolic 1mM-R(0.75ml) pH=6.4 to 6.9phosphate buffer	λmax=530nm 1 to 20 ppb S=30pg Cm-2	$Th, Cu^{II}, Ni, Fe^{III}$,& Cr^{VI} interfere. All except Cr^{VI} can be masked with nitrilotri-acetic acid	Heating 90min at 60° cooling 5 min in H_2O Waiting 15 min Reagent blank needed.Analysis of wastewater.	44
39	Catechol Violet & Alizarin red S (C.I. Mordant Red)	Aqueous	1) pH =.2.7 2)pH = 3.8	1)λmax=540 nm 1 to 50µM 2)λmax=480nm 0.5 to 5ppm		1)1:1 complex C.V.=1.4%at 1.7 µg ml-1 2)1:2 complex,C.V. =5.5% For soln.of pH 1.5to 2.0, neutralisation & boiling for 10 min are necessary to decompose polymeric molybdates before extraction.	45
40	Bromopyrogallol red (I)+Hexadecyl pyri-dinium chloride	Aqueous	1)0.05 to 5M-H_2SO_4 i.e. 40 µ M in I + 2) 0.2 mM in II	λmax=630nm, ϵ =80,000 0.08 to 1.4 ppm at pH=1	W^{Vl} interfere Fe^{III} is masked ascorbic acid	1:2:2 complex C.V. < 9.1% Analysis of steel soyabean,wheat etc.	46
41	2,6,7-Trihydroxy-9- (2-nitrophenyl)-Xanthe -3-ones.II and Diaoti-pyrinyl methane(I)	$CHCl_3$	0.5 to 1.5M-HCl,0.6% of I and 0.2mM in II	λmax=490 nm, ϵ =131,000 at optimum of 530 nm 0.07to 0.6 ppm	-	1:3:2 complex, method used to determine Mo in Fe-Ni-Mo mognetic films	47

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1	2	3	4	5	6	7	8
42	Thiocynate and Rhodamine 6G(C.I. Basic Red 1)	Aqueous	0.55 to 0.8M HCl,3% KSCN(5ml),Aq.0.01% R(5ml)1%gelatin(1ml)	λmax=570 nm 0.04 to 0.25 ppm	Zn & Co	Waiting 1 hr.Reagent blank needed	48
43	α and β molybdosilicic acid I& II	Butanol	2M H_2SO_4	I- λmax=700nm, ϵ =64.40 II λmax=790nm ϵ =18,150 for I at 790nm ϵ =5150and For II at 700nm ϵ = 9460	-	C.V. < 4% for 2.6 to 95μM-I and 5 to 47 μM II	49
44	Pyrogallol red^{II} and Hexadecylpyridinium chloride (I)	Aqueous	pH=4.7 acetate buffer 10mM-I,1mM-II(1.5ml) in methanol	λmax=610 nm S=0.0028 $\mu g/cm^2$ upto 3 ppm	Al, Te^{III} and Th^{IV} need masking	Waiting 50 min.Reagent blank needed	50
45	Thiocynate and nitron	$CHCl_3$	3-4M-HCl,10% $FeSO_4$ soln(1ml),10% ascorbic acid(10ml),10% KSCN (2ml)0.5g/L Nitrogen sulphate soln(10 ml)	λmax=465 mm 1.2 to 12ppm	Mn^{VII},Ti^{IV} and peroxide ions interfere	Shaking 1 min. Waiting 20 to 40 min,Reagent blank needed std.deviation =0.890± 0.005	51
46	1-Nitroso-2-napthol	Chloroform +Isoamyl alcohol (1:1)	2 to 3M-HCl,0.5mMR	λmax=380nm, ϵ=2500 2 to 20 ppm	-	1:1 complex,C.V.= 8.7% scrbing the extract with NaOH to remove the reagent is needed Analysis of steel.	52
47	Bromanilate	Aqueous	pH <6;3M or 1.4M $HClO_4$	λmax=340 nm	Zr,Hf,U^{VI} Cr^{VI},V^{V} W^{VI},Sn and Bi interfere	1:1 complex	53
48	Phenylhydrazine sulphonic acid	Aqueous	Acetic acid anhy (10ml)+4% aqueous R(5 ml)	λ max=510nm 0.6to 6 ppm S=12 ng Cm^{-2}	-	Warming necessary	54

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	2	3	4	5	6	7	8
9	1,10-Phenathroline and Bromopyrogallol red	Aqueous	pH=4	λmax=600 nm, ϵ=27,000 upto 0.8 ppm	-	1:2:2 complex	55
0	Thiocynate mepazine (pecazine) hydrochloride	$CHCl_3$	10M-HCl(2ml),Aq. 10% aseorbic acid (2ml)aq.10% KSCN(5ml) 0.02M-R in $CHCl_3$	λmax=465 nm,Analytical range=0.9 to 5.4ppm S=5.4 ng Cm^{-2}	-	Waiting 15 min Reagent blank needed Analysis of steel	56
1	4-(2-thiazolylazo) catechol	Aqueous	I-40% acetone medium pH=3.2to3.8 II pH=5.4to 6.2	λ max II=530 nm ϵ =54,000 2 to 20 μM	-	I - 1:1 complex II - 1:2 complex	57
2	2,2'-Dihydroxy benzophenone thio semicarbazone	Aqueous	0.5M HCl,(20ml) 0.2% ethanolic R(20ml),2% $SnCl_2$ soln(0.05 ml)	λmax =500 nm 1.20ppm	Prior removal of interfering ions by dithizone needed	1:1 complex waiting 8 min	58
3	Phenylfluorone	$CHCl_3$	1M-$HClO_4$(3ml)1mM R in ethanolic 0.06M HCl(2ml) Ethanol(1 ml)	λmax=518nm,0.12 to 0.96 ppm	Zr and Nb	-	59
4	ϵ-Caprolactun +SCN	Aqueous	2 to 7M-HCl,0.3M KSCN,35 mg ml^{-1} of solid R	λmax=475nm, ϵ=20,000 0.3 to 18 μg ml^{-1}	Nb,Cu,Pb,Sn^{II} and W^{VI}	1:4:5 complex C.V. $<$ 2.7%	60
5	N'-(4-chloro-phenyl)-N-(4-chloro-o-tolyl) -N'-hydroxybenzamidine hydrochloride +SCN	Benzene	1:5 to 4.5M-HCl	λmax=470nm, ϵ=4500 2 to 20 ppm	-	-	61
6	2-Methoxy-N-P-tolyl benzohydroxamic acid	Isoamyl alcohol	pH=2.5 to 3.5	λ max=355 nm,0.3 to 11 ppm	V(V)is masked with ascorbic acid		62
7	2',3'4'-Trihydroxy azobenzene-4-sulphuric acid	Aqueous	10to150mM in HCl H_2SO_4, H_3PO_4 or HNO_3	λmax=460nm ϵ=18,500 0.2 to 3.8 ppm	-	1:2 complex,the method hasbeen used for determining 37to 325 ppm of MO C.V. $<$ 8.3%	63

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1	2	3	4	5	6	7	8
58	Rasacetophenone oxime	Aqueous	0.1M soln.in aq.50% ethanol,4mM-HCl	λmax=400nm upto 230 ppm	Oxalate,tortrate citrate,acetate edta,borate, PO_4^{3-} and Al interfere	-	64
59	Chlorpromazine hydrochloride	$CHCl_3$	10M-HCl,or H_2SO_4 (2ml)Aq.30% KSCN (3ml),Aq.10% ascorbic acid(2ml),After 10 min 0.02M-R	λmax=465 nm 0.5 to 5 ppm	Coloured metal thiocynates complex interfere	Waiting 10 min shaking 2 min Reagent blank needed,1:1:4 complex	65
60	Benzohydroxamic acid	Hexanol	pH = 2, 0.05M-R	λmax=370nm ϵ =2200 0.5 to 40ppm	V^V,Ce^{IV},Ti^{IV} and Fe^{III} interfere	1:2 complex	66
61	O-Hydroxhydroquinonephthale in +Surfactant	Acid medium	3.5%LT-221 surfactant soln(2ml),1mM-R (1ml),pH=1.8 (Walpode buffer soln)	λmax=520 nm, ϵ =130,000 S=0.7ng Cm^{-2}	-	Reagent blank needed	67
62	Sodium 2'-bromo -4',5'-dihydroxyazobenzene-4-sulphonate (I)+Cetyltrimethyl ammonium chloride	Aqueous	pH =1.6(HCl-Na-acetate)2mM-I(3ml) 0.01M-II(3.5ml)	λmax=525nm upto 28 μg, S=1.5 ng Cm^{-2}	W^{VI} interfere Fe^{III}, Sb^{III},Ti^{IV}, Zr^{IV},V^V are masked with EDTA NaF or ascorbic acid	Ternary complex Analysis of steel.	68
63	Benzoinoxime	Chloroform	NaCl(Sat)+HCl Extracted into chloroform Mo determined by thiocynate method	λmax = 490nm	-	Shaking necessary.Waiting 1hr.	69
64	Hexamethylphosphoramide	$CHCl_3$	400 mg of NH_4SCN M HCl, 1 ml-R	λmax=460 nm 0.75 to 5 ppm	Prior extraction of $Fe(SCN)_3$ with TBP Nb^{IV} and Ti^{IV} masked with NaF(Cu^{II} with Thiourea	Heating 15 min Reagent blank needed.Analysis of alloy	70

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1	2	3	4	5	6	7	8
65	Deta(1,2-diamino cyclohexane-NNN'N' tetra-acetic acid	Aqueous	pH=3 to 7,0.5N-H_2SO_4 Hydrazine sulphate (0.2g), at pH=5 add ≃ 5mMR	λmax=300nm	-	2:1 complex Waiting 5 min at 100°	71
66	3-Hydroxy-2-methyl 1-phenyl-4-pyridone	$CHCl_3$	pH=1 to 3.2,0.2 M soln R in $CHCl_3$	λmax=317 nm, ϵ=25,000 0.5 to 5 ppm	Prior extraction of U^{VI} with the same reagent of pH V interfere	1:2 complex Reagent blank needed	72
67	4-Butyrylpyrogallol (2'-3'.4'-Trihydroxy butyrophenone)		1)I-pH=5.2 to 6.5	1)λmax=355nm extinction is measured at 410 nm 0.4 to16ppm	Prior extraction of Fe^{III} necessary	1:2 complex	73
			2)With I in presence of hydroxylamine pH 4.2to 5.2	2)λmax =350 nm 0.4 to 40 ppm			
68	Dimethylanilinium Perchlorate	Dichloro-ethane	3to 4M-$HClO_4$ of H_2SO_4 0.5 to 0.6M-SCN^-, 300 to 400 fold R	λmax =470nm, ϵ=15,000 1 to 10ppm. S=0.0064 µg Cm^{-2}	-	Analysis of steel Relative error 0.18-0.62	74
69	4-Propionylpyrogallol(2',3',4'-Trihydroxypropiophenone)	Aqueous	pH=2.5 to6(.5.6)	λmax=390nm, ϵ = 8635 0.2 to 12 ppm	Fe^{III}, U^{VI} & Cr^{III}	1:2 complex Analysis of alloy Fe+Ni+Mn+Co	75
70	5-Chloro-8-hydroxy 7-idoquinoline	$CHCl_3$	pH=1 to 2 acetate HCl buffer 2.5mM-R in $CHCl_3$ (10 ml)	λmax=392 upto 6 ppm	-	1:2 complex shaking 5 minReagent blank needed	76

Contd..

1	2	3	4	5	6	7	8
71	2-Methoxy-N-O tolylbenzohydro xamic acid	Isopentyl alcohol	pH=1.5 to 2.5,0.1m-KH phthalate (5ml),0.1M-R	λmax=350nm 0.5 to 10.5ppm	—	Shaking necessary method canbe used to determine Mo in steel	77
72	Isopropylnoradre naline(Isoprenaline)	Aqueous	pH> 4 (5.5)	λmax=400nm, ϵ 4800; 0.5to20ppm	Fe^{III}, U^{VI}, and Ti^{IV}	1:2 complex	78
73	2-Aminobenzene thiol	$CHCl_3$	pH=2.0,2% 2-R soln in $CHCl_3$ (5ml)	λmax=700 nm 0.5 to4.5 ppm	Bi^{III}, Sn^{II} interfere. Prior extraction of Ni, Fe^{III} and V^{V} masked with ascorbic acid and $NH_2OH.HCl$	Shaking 5 min stability=2 h.	79
74	NN-Diethyl aniline (I)perchlorate	Dichloro- ethane	3 to 4N-$HClO_4$ or H_2SO_4 0.5 to 0.6M-KSCN, excess R	λmax=470nm, 1 to 10ppm	-	Analysis of steel Relative error = ± 3%	80
75	2-Hydroxy-5-Metho- xybenzaldoxine	Aqueus	pH= 3.2 to 3.8	λmax=370 nm 5 to 70ppm at 370 nm at λ max 400 nm, 5 to 110 ppm	-	Analysis of oil 1:1 complex	81
76	Potassium propylxa nthate	CS_2	2M-HCl,pH ≃ 1:1 HCl glycine buffer 1% aq.R(1ml)	λmax= 510 nm 1-14 ppm	-	1:2 complex at 20°	82
77	OO-Bis(α-(3-methyl -5-OXO-1-phenyl-2 pyrazolin-4-ylidene-P tolyl)phosphorodithioate	$CHCl_3$	3.5 $HClO_4$, Aq.10mm R	max=415 nm 2 to 12 ppm	-	Shaking necessary for 2 min stability = 3 h.	83
78	Trioctyl arsin oxide	Benzene	5 to 7N-HCl, H_2SO_4 and HNO_3, 0.05M-0.1M,R in benzene, pH-2to3	-	-	The D decreases in the order H_2SO_4 > HCl > HNO_3	84

Contd..

1	2	3	4	5	6	7	8
79	Phenylflurone	$CHCl_3$	-	λmax =515 nm, upto 10 ppm	-	Separated from Se and Te	85
80	Carboxygallanilide	-	pH=4.4 to 6.5 (acetate buffer)	λmax at U.V.region at ~ 400 to520 nm, ϵ = 1500 at 490 nm	V interfers W, Fe,Ni,Ti, Zr,Nb and Ta are separated as hydroxides	2:3 complex	86
81	Catechol and butyl triphenylphosphonium bromide	$CHCl_3$	-	λmax=370 nm	-	Ternary complex. Method is suitable for determining 0.01% of Mo	87
82	Tetraphenylarsonium and Tetraphenyl phosphonium	$CHCl_3$	Ascorbic acid+HCl or H_2SO_4+SCN+R	λmax=470 nm 0.05 to 0.1mM	Ti masked with fluoride	C.V. 0.2 to 2%	88
83	2,3,5-Triphenyl tetrazolium chloride	Dichloroethane	pH=0.5 KCl-HCl buffer 0.3M catechol(5ml) 4mM-RI(0.5ml H_2O(1ml) R-II-(10ml)	λmax=640 nm 2.5 to 15 ppm	-	Shaking 30 ,waiting 10 min C.V.=2.97% for 10 determinations of 15 µg.	89
84	Thiocynate-octyl (α-anilinobenzyl phosphonate complex	$CHCl_3$	10M-HCl(3ml),30% aq. KSCN(2ml),10% ascorbic acid(1ml),After 10 min 0.02M R in $CHCl_3$(5 ml)	λmax=470 nm 0.7 to 28 ppb	-	Waiting 5 min. shaking 2 min.	90

Contd..

1	2	3	4	5	6	7	8
85	Toulene-3,4-dithiol	Aqueous	6M-HCl,TBP std.with 6M-HCl(5ml),Anhyd acetic acid(25 ml) H_3PO_4(2ml),R(in 100ml of 10% NaOH(5ml)+ 1 g of mercaptoacetic acid	λmax=705 25 to 100µg	-	Shaking 5 min.Waiting 3 hr.	91
86	5,7-Dibromo-8-hydroxyquinoline	Organic phase	pH=2,50µM-Na_2MoO_4 (10 ml)	λmax=360 nm	-	Waiting 6 min	92
87	3,3'-4,4',5-pentahydroxybenzophenane	Aqueous	pH >5.2	λmax=375 nm,extinction measured at 410nm. ϵ =15,800,0.2to 16 ppm.	Al,U^{VI} or Ti^{IV} & Cu^{II} interfere.Prior extraction of Fe^{III} with AA+pyridine at pH 4.6	---	93
88	Benzohydroxamic acid	Hexanol	aq.0.1M soln.of R (10 ml)	λmax=370nm	V,Ce^{IV},Ti^{IV} & Fe^{III} interfere	-	94
89	Hydroxylamine poly hydric phenol(2',3',4'-Trihydroxypropiophenone(I),2,3,4-Trihydroxy benzophenone(II),or2,3,3',4,4',5'-Hexahydroxybenzophenone(III)	-	pH for I&II =4.6	λmax for I& II= 410nm, λmax for III=420	-	I and II Ternary complex I,II &III can be used to determine Mo in ferromolybdenum after extn of Fe.	95

Contd..

1	2	3	4	5	6	7	8
90	Bromopyrogallol red and Zephiramine	Aqueous	0.16 to 0.24M-HCl, 10mM-R (1.5ml), 0.03% bromopyro gallol red soln(1ml)	λmax=629nm ϵ=55,000 2 to 25 µg per ml soln S=1.7ng Cm^{-2}	Sb^{III}, Fe^{III}, Sn^{IV} Zr, Hf V^{V}, Cr^{VI} and W^{VI} interfere	1:1 complex, waiting 20 min. Analysis of steel	96
91	Thiosulphate complex	Isoamyl alcohol	10M-HCl(2ml), at 10to15° isoamyl alcohol(10ml), $Na_2S_2O_3$(2ml)at 10to 15° drops of Br	λmax=475 nm	-	Shaking 2 to2.5 min	97
92	Antipyrinyl-bis-(4-diethyl aminophenyl) methanol	Aqueous	30% aq.H_2O (0.5ml), 2N HCl(4.5ml).0.1g ascorbic acid, thiourea(0.5g), 50% NH_4SCN (5ml), 0.5% galatin soln.(0.5ml) 0.4%-R in N-HCl(1ml)	0.12 to 3.2 ppm	Zn interfere	1:3 complex, stability 3h, temp 16 to 19°, waiting 15 min. Reagent blank needed	98
93	Gallein and Papavarine		pH = 2.7	λmax=530nm ϵ=16,000 In presence of papaverine, λmax =600nm, =23,000	V and W interfere	Ternary complex C.V.=6.2,4.8 & 2% Detection limit = 0.06 ml^{-1} Natural water analysed	99
94	Thiocynate and Antipyrine	$CHCl_3$	2.7 to 9M-HCl, or 45 to 5.4M H_2SO_4	λmax=440nm, ϵ = 19,000. 0.1 to 130 µg per 5ml extract	Fe^{III}, Cu^{II}, Ti^{IV} Nb^{V}, Ta^{V}, Bi^{III}, W^{VI}, Cr, U.V. and Co are masked	Ternary complex method is applicable to steel.	100
95	Quinoline+ Thiocynate	Nitrobenzene	Quinoline in 0.2 M-HCl, 6M-KSCN(10ml), Conc.HCl(7ml)H_2O(3ml)	λmax=470nm	Co, Cu, Fe and Ti are removed as their hydxides	Analysis of steel	101

Contd..

1	2	3	4	5	6	7	8
96	Triethylamine +SCN	Chloro-form	2.7to 6.5M-HCl,or 1.3 to 4.5M H_2SO_4,120,000 fold to 130,000 fold excess of SCN and a 650 to 660 fold excess of triethylamine	λmax=460 nm, ϵ =28,000	W,Cu,Ta,Ti, and Nb need masking	Soil analysis	102
97	Salicylohydro-xamic acid	Isoamyl alcohol	pH=3,KH pthalate HCl buffer, 0.01M R	λmax=345 or 360 nm, ~65 to 215ppm silicate rocks	-	Shaking 5 min.Reagets blank needed.Rock analysis	103
98	Diphenylgua-nidine+SCN	$CHCl_3$	0.9M to 3M-H_2SO_4, 0.03M-R and 2 to 4M SCN -	λmax=470nm, ϵ =21,000 0.7to 70µg per 10 ml S=0.2µg Cm^{-2}	-	0.2 to 1% in steel	104
99	Phenylfluorone and (Hexade-cylpyridinium chloride)	Aqueous	pH=.15 NaCl-glycine -HCl buffer,10mM-R_2 (1ml), 2mM-R_1-(2ml)	λmax =540 nm	-	Temp 45°,Waiting 30 min.Reagent blank needed	105
100	Stilbazo + Zephiramine	Aqueous	pH=3.9 acetate buffer 5% R_2	λmax=535 nm upto µg	Al,V,Ti and Zr masked with F^-	Within 2 min Reagent blank needed.Steel dissolution	106
101	2,6,7-Trihydro-xy-9-(4-nitro phenyl)xanthen 3-one	TBP	Ethanolic 0.5% R	λ max=530 nm ϵ =45,000, 1 to 75 ppm	-	1:2 or 1:3 complex stable for 1h steel analysis	107
102	4-Galloyl pyrogallol	Aqueous	pH =6.04	λmax=420 nm 1 to 20 ppm	-	-	108

Contd.

1	2	3	4	5	6	7	8
103	1,1-Dianti-pyrinyl heptane catechol	Dichlo-roethane	0.4M-catechol(2.5ml) pH=2.0,mM-R(10 ml)	λmax=440 and 640nm,5μM to 0.2 mM	Ascorbic acid used toprevent interference of Al,Ti,Sn Bi and Fe^{III}	Shaking 1 min Waiting 2 h.	109
104	K-Ethylxan-thate	Acetoph-enone	10M-HCl,aq.1% K.ethyl Xanthate(2ml),aq.5% NH_4SCN(2ml)	λmax=380 or 470 nm	-	Shaking 2 min Reagent blank needed.Multiple extraction.	110
105	Green Mo(V) species by Reduction	Isoamyl-acetate alcohol	5.5-HCl,Redn.by hydra-zinium sulphate(1 mg) 7M-HCl	λmax=720 nm, 0.08 to 5.4 ppm	C_o interfers	Reagent blank needed.Analysis of sample	111
106	Quinalizarin	Aqueous	pH=5,5 fold excess of R, 50% ethanolic medium	λmax=540nm,1 to 10 ppm.S=0.0077 μg Cm^{-2}	Many foreign species interfere	1:1 complex, waiting 30 min Max.error = 0.5% for 5ppm	112
107	4-Methyl-pentane-2-ol ~~Benzene~~	Benzene	Aq.M-HCl +Licl,50% R in benzene,and deter-mined as thiocynate	λmax=465 nm	Ti and Sn interfere	Method applica-ble tothe analysis of std. cast iron samples	113
108	2-Mercapto-benzo-γ-thiopyrone+ Ammoniumthio cynate	Acetophe-none	10M-HCl(2ml),5% NH_4SCN, 0.1% aq.R and 11.5% $SnCl_2$ soln.	λmax=470 nm, S=0.05 μg Cm^{-2}	F^-,$S_2O_3^-$,Ni^{2+} Cu^{2+},Ag^+ and Co^{2+}	Multiple extract-ion Reagent blank needed steel analysis	114
109	Pyrogallol & Aniline	Chloroform +isoamylalcohol (1:1)	pH=3 to 4	λmax=410 nm ϵ =7000,10-300 g	-	Ternary complex	115

Contd..

1	2	3	4	5	6	7	8
110	8-Hydroxy-quinoline +Pyridine	Pyridine	6N-H_2SO_4,3% hydrazine sulphate soln(4 ml), 6% R (2ml),pyridine (10 ml)	λmax=405 nm, 0.8 to 24 ppm	Fe and Cu interfere.Prior pptation of Mo with benzoin α-monoxime	Reagent blank needed	116
111	Chloropromazine,methoxyphenothiazine or di	Cholroform	M-H_2SO_4,1.5M-NH_4SCN	λmax=465 nm	Co,Cu,Bi,Fe, Ti,W and U^{VI} interfere	1:1 complex	117

by gentle boiling and simultaneous stirring for 3 min. 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 in a oven. It was finally weighed as $MoO_2(C_9H_6ON)_2$. Suitable concentration containing 100 µg per ml was prepared as needed by diluting the stock solution with distilled water.

Reagent Solution :

A 0.5 gm of the reagent 5-Methyl SAT was dissolved in 100 ml of hot ethyl alcohol to obtain 0.024 M reagent solution. The solution is quite stable towards light and heat. It is soluble in hot ethyl alcohol and can be kept over a week period. All solutions used in study of diverse ions were prepared from AR grade chemicals.

Apparatus :

Absorption measurements were made with Carl-Zeiss(JENA) spectrophotometer using 1cm glass cells.

General Procedure :

To an aliquot of the solution containing upto 500 µg of molybdenum, requisit amount of HCl and 5 ml of 0.024 M alcoholic reagent were added so as to have 3M acidity and 4.8×10^{-3}M reagent respectively in a 25ml volume. The reaction mixture was heated on water bath for 20 min. It was then cooled and made upto 25 ml with distilled water. The absorbance of the red complex was measured within 50 min at 510 nm against the reagent blank prepared in similar manner.

RESULTS AND DISCUSSION

Spectral Properties :

Fig.1 shows the absorption spectrum of Mo-5-methylSAT complex containing 16 ppm of molybdenum and 4.8 x 10^{-3} M reagent at 3M HCl using reagent blank. Absorption measurements were made in the spectral range 460-700 nm. The spectral curve indicates that the complex exhibits absorption maximum at 510nm, at which wavelength the ligand has slight absorption. The complex is not extracted by benzene, nitrobenzene, chloroform or carbon tetrachloride. With MIBK and amyl alcohol the red colour changes to yellow green. Benzyl alcohol extracts the red violet complex but the solution is very unstable.

Effect of Acidity :

In order to find out the optimum concentration of hydrochloric acid required for the full colour development of molybdenum complex as a means of acidification hydrochloric acid was varied in the range 1-8M. The curve in the fig.2 indicates that the absorbance of the complex at 510 nm containing 16 ppm Mo and 4.8 x 10^{-3} M reagent was found maximum and constant at 3M-HCl At less than 3M HCl concentration ,precipitation occurs. Whereas decrease in absorbance, occured at greater than 3M acidity. Hence rigid control of 3M HCl is necessary for further studies.

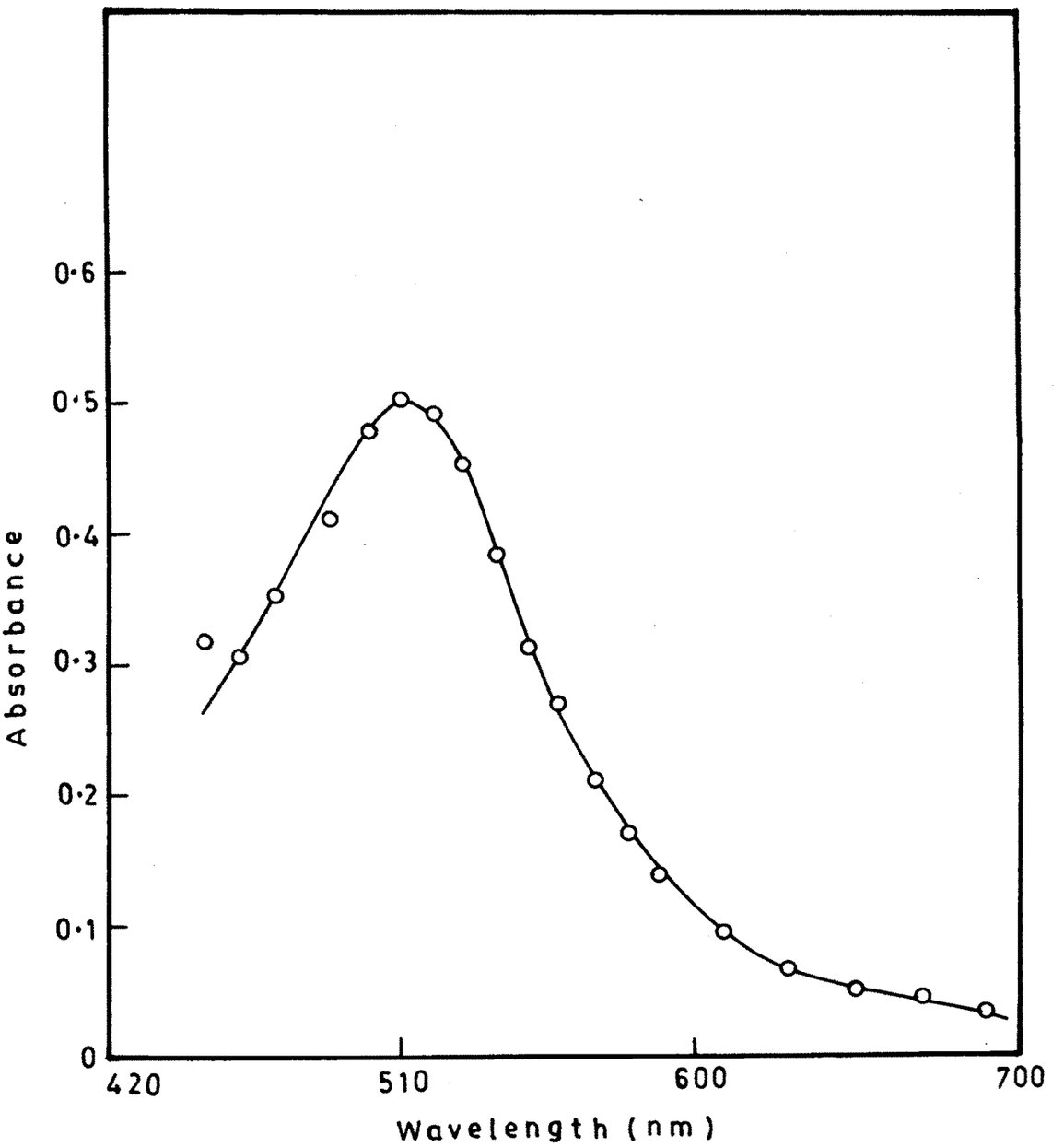

Fig.1 — SPECTRAL CHARACTERISTICS OF Mo(V) — 5-METHYL SAT COMPLEX.
Mo(V) : 16 ppm

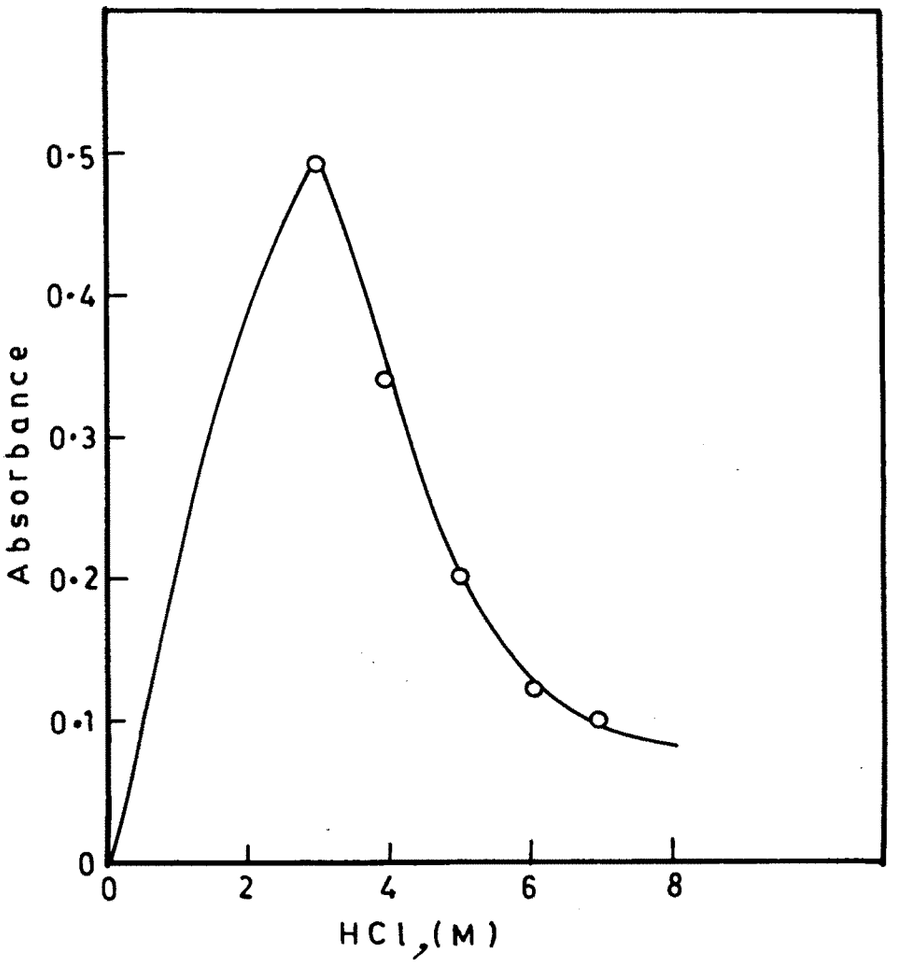

Fig. 2 — EFFECT OF ACIDITY .

λmax. = 510 nm

Mo(V) = 16 ppm

Effect of Reagent Concentration:

Solutions containing the same amount of molybdenum(16ppm) but different amounts of the reagent varying from 1.0 -8.0 ml of 0.024 M alcoholicreagent were prepared. The colour was developed as outlined in the general procedure and the absorbance of the complex was measured at 510 nm against the simultaneously prepared reagent blank. The results of studies as shown in Fig.3 indicate that 16 ppm of molybdenum required a minimum of 5 ml of 0.024 M reagent solutions (25 mg of reagent dissolved in 5 ml of alcohol). At this reagent concentration the reagent to metal ratio in terms of moles is approximately 30:1. At high reagent concentration the turbidity was formed and the absorbance could not be measured.

Effect of time of heating and stability of the Complex:

The development of the colour of Mo-(V)-5-methyl SAT complex containing 16 ppm of Mo and 5 ml of 0.024 M alcoholic reagent at 3M HCl was carried out by heating on water bath over a period from 1-60 min. The complex was measured at 510 nm against the reagent blank treated in a similar manner. It was observed that 20 min heating was sufficient for full complexation. However, excess heating is not detrimental.

The absorbance of the complex at 510 nm remained constant upto 50 min after the development of the colour. Hence the complex should be measured within 50 min of the colour development.

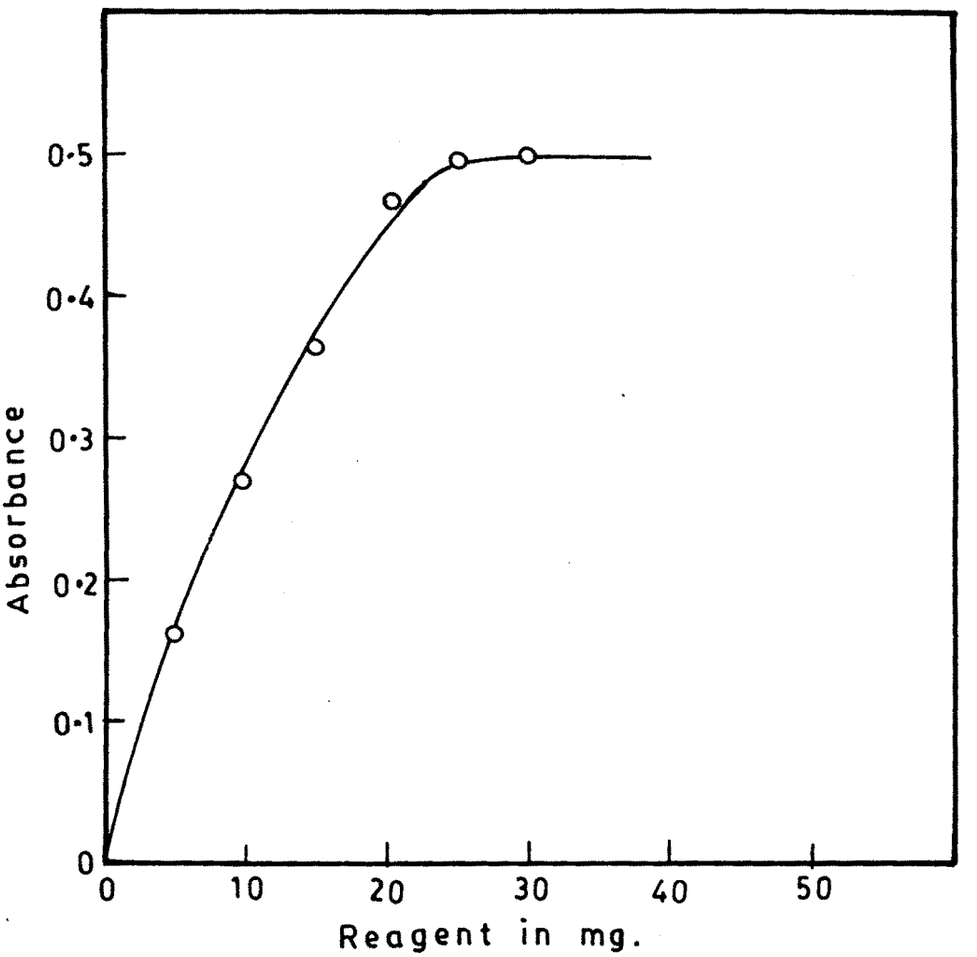

Fig. 3 — EFFECT OF REAGENT CONCENTRATION.

Mo (V) : 16 ppm

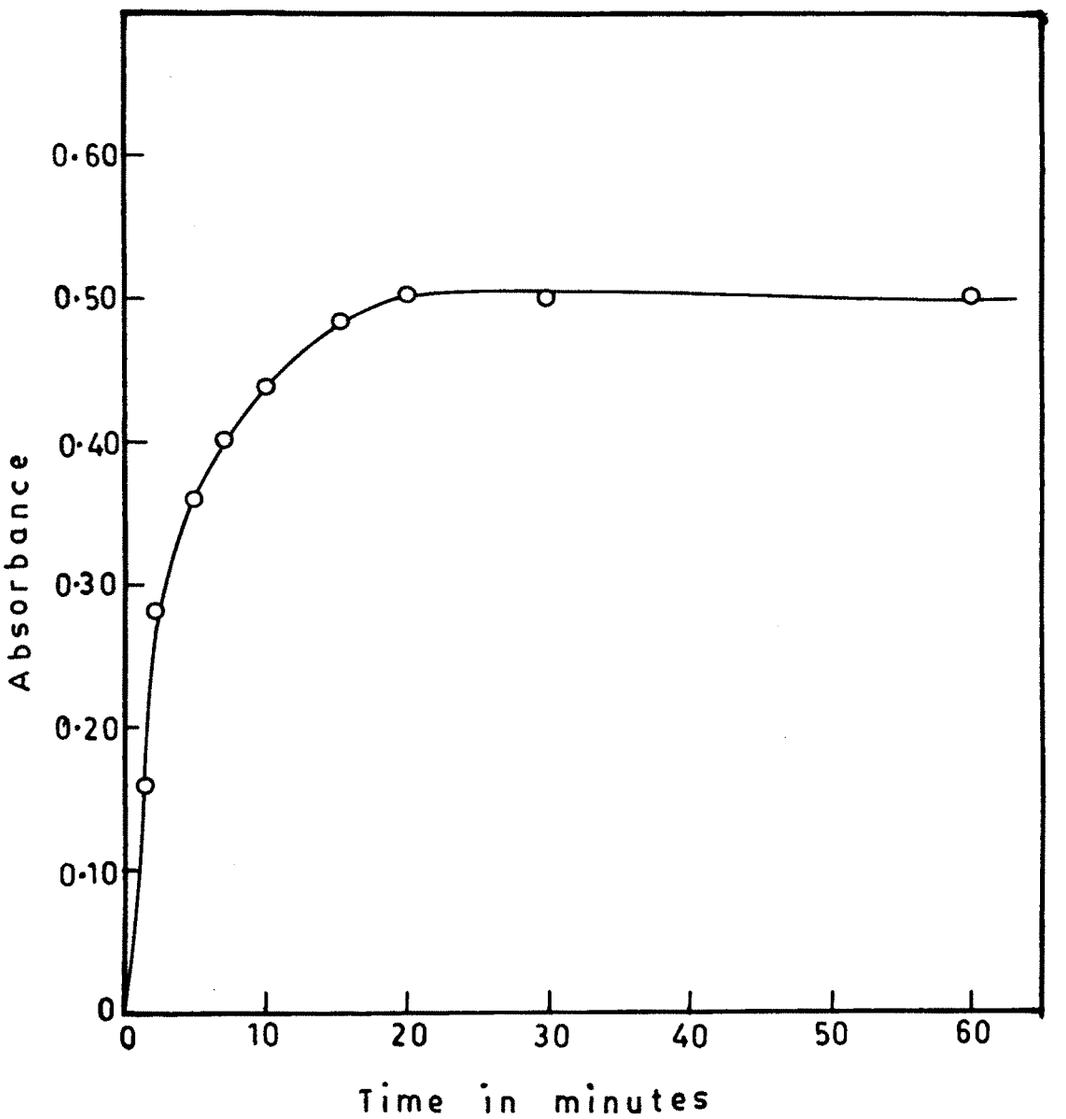

Fig. 4 — EFFECT OF TIME OF HEATING .

Mo (V) : 16 ppm

Effect of Alcohol :

Inorder to find out the amount of alcohol needed during the complexation of M_o(V)-5-methyl SAT complex,the amount of alcohol was varied between 1 to 15 ml in the aqueous phase of 25 ml. It was found that atleast 4 ml alcohol is required for full complexation and there is no significant effect on the absorbance when from 5 to 10 ml alcohol in 25 ml aqueous phase was present (Fig.5).

Study of Validity of Beer's Law :

The solution containing different amounts of M_o in the range 50 to 600 µg were used for the study of the validity of Beer's law. The colour was developed as per the recommended procedure using 4.8×10^{-3} M reagent and was measured at 510 nm against the reagent blank. The curve in Fig.6 shows the linearity between absorbance and metal ion to be in the range 0.5 -20 ppm of M_o(V).

Composition of the Complex:

In order to establish the composition of the complex,the equimolar solutions of metal and ligand 8×10^{-5}M were used. 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 3M with HCl, and the colour of the complex was developed as per the recommended procedure and the absorbances of the solutions were measured at 510 nm against reagent blank. The plot of the absorbance against the mole fraction of the reagent indicated the existence of 1:1 complex with respect to metal and ligand.(Fig.7).For mole ratio method, solutions containing the same final molybdenum concentration 8×10^{-5}M and different amounts of the reagent ranging in concentration from 4×10^{-5} to 4×10^{-4}M were prepared maintaining.

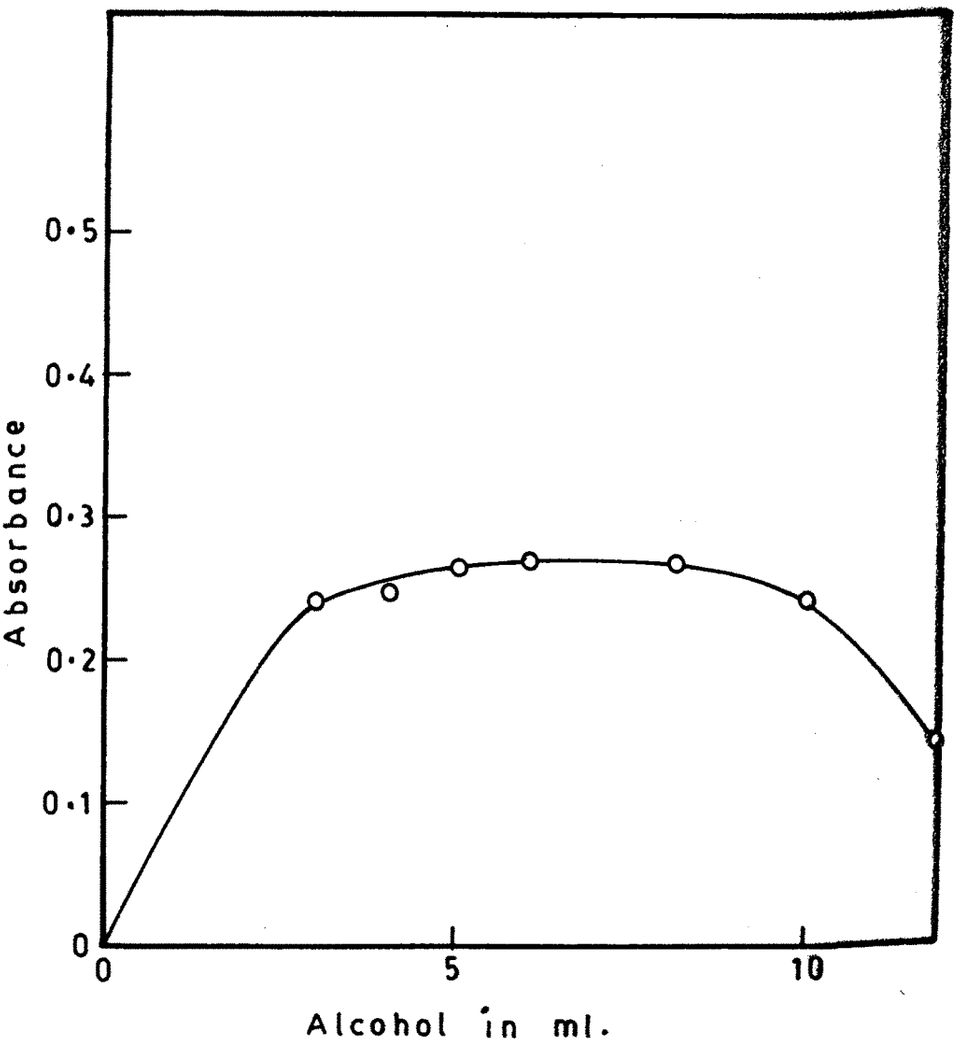

Fig. 5 — EFFECT OF ALCOHOL.

Mo(V) : 8 ppm

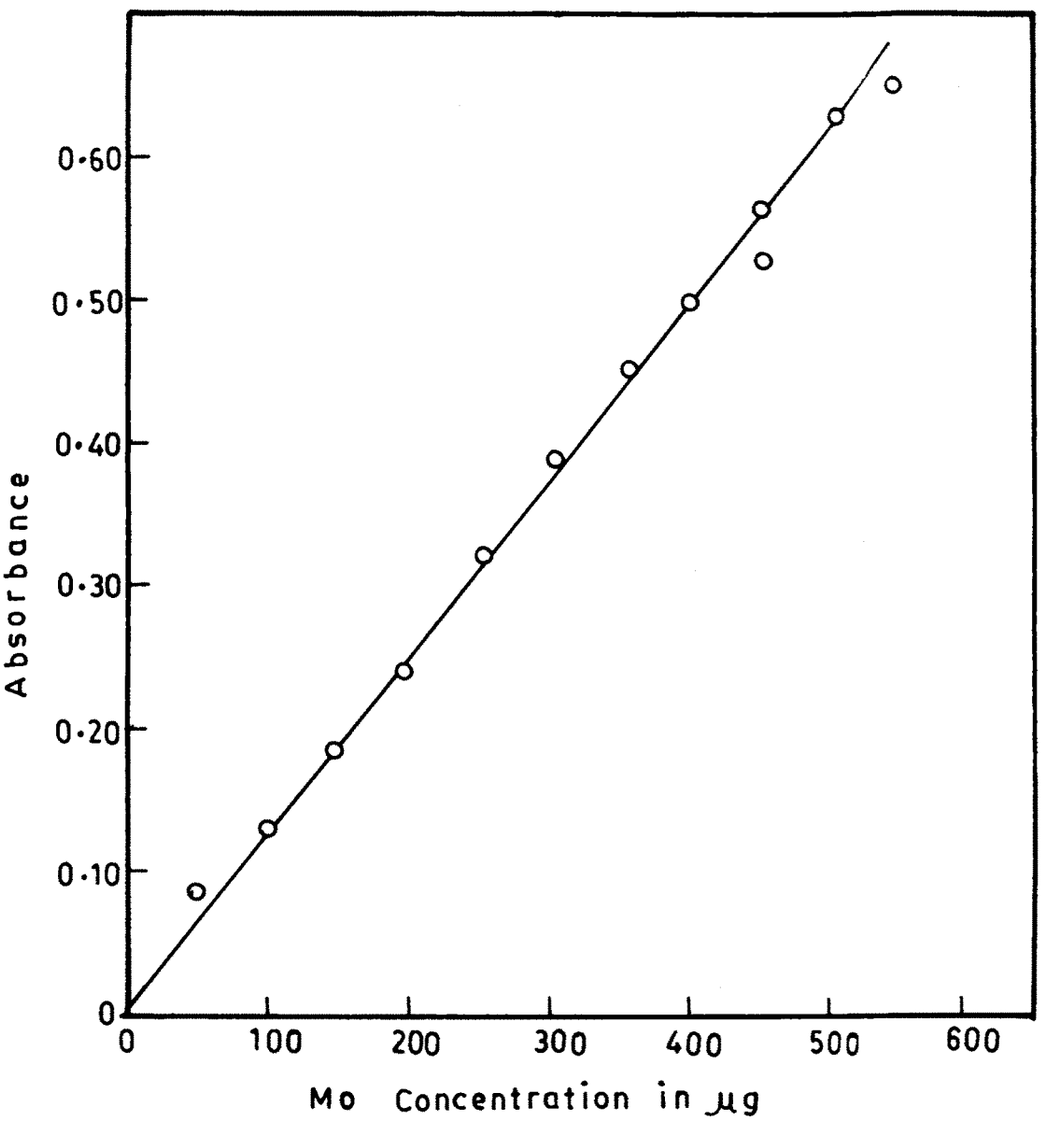

Fig. 6 – VALIDITY OF BEER'S LAW FOR Mo(V)–5–METHYL SAT COMPLEX.

$[R] = 4{\cdot}8 \times 10^{-3}$ M

$\lambda max = 510$ nm

3 M acidity with respect to HCl. The colour of the complex was developed as per the recommended procedure and was measured at 510 nm against reagent blank. The plot of the absorbance against the reagent to metal ratio (Fig.8) confirms the results obtained by application of Job's method.

Reproducibility, Accuracy and Sensitivity data :

For study of the reproducibility and accuracy of the method absorption measurements with ten different identical solutions containing 16 ppm molybdenum were performed as in the outlined procedure and concentration determined using the calibration curve. The results are shown in Table-2. 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 in each case and then standard deviation was calculated. From the standard deviation σ, the reproducibility of the results with 95% confidence limit was calculated. The Sandell sensitivity of the reaction (Sr) as calculated from Beer's plot was found out to be 31 ng/cm^2.

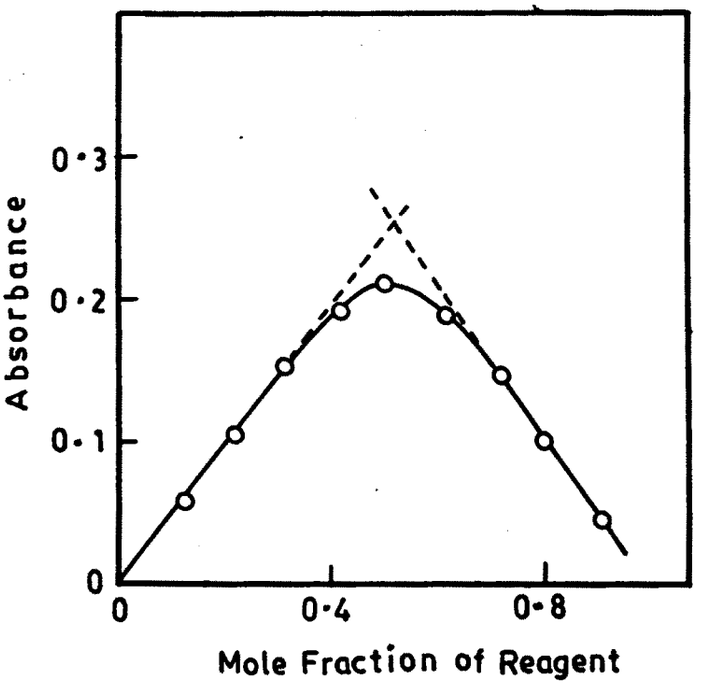

Fig. 7 —

JOB'S PLOT

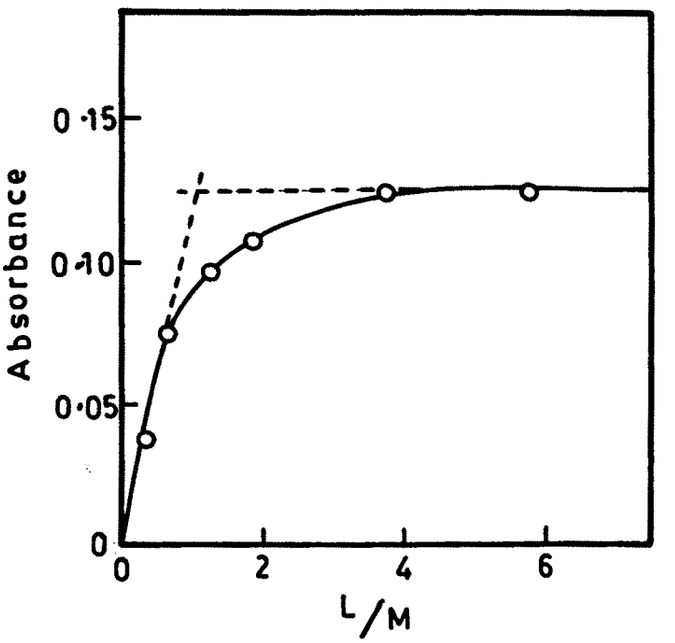

Fig. 8 —

MOLE RATIO PLOT

Table 2 : Precision and Accuracy of the Method
Amount of Mo taken = 16 ppm.

Absorbance observed	ppm of Mo found, x	$X - \bar{X}$	$(X-\bar{X})^2$
1) 0.522	16.00	00.00	00.00
2) 0.515	15.80	- 00.20	0.0400
3) 0.522	15.95	- 00.05	0.0025
4) 0.525	16.15	+ 00.15	0.0225
5) 0.522	16.02	+ 00.02	0.0400
6) 0.516	15.85	- 00.15	0.0225
7) 0.515	15.80	- 00.20	0.0400
8) 0.527	16.18	+ 00.18	0.0324
9) 0.528	16.20	+ 00.20	0.0400
10) 0.523	16.05	+ 00.05	0.0025
	160.00		0.2424

Average value $(\bar{X}) = \frac{160}{10}$

$= 16$

$$\text{Standard deviation} = \sqrt{\frac{(x_1-\bar{x})^2+(x_2-\bar{x})^2+\cdots(x_n-\bar{x})^2}{n-1}}$$

$$= \sqrt{\frac{0.2424}{9}}$$

$$= 0.164$$

Reproducibility with 95 percent confidence limit

$$= \bar{X} \pm 2.26 \times \frac{\delta}{\sqrt{n}}$$

$$= 16 \pm 2.26 \times \frac{0.164}{10}$$

$$= 16 \pm 2.26 \times \frac{0.164}{3.16}$$

$$= 16 \pm 0.117$$

Molar Extinction Coefficient :

$$\epsilon = \frac{A}{Cxl}$$

$$= \frac{\text{Absorbance}}{\text{ppm}} \times 1000 \times \text{At wt.}$$

$$= \frac{0.50}{16} \times 1000 \times 96$$

$$= 3000 \text{ l mole}^{-1} \text{ cm}^{-1}$$

from graph = Slope x 1000 x 96

$$= \frac{0.15}{4.6} \times 1000 \times 96$$

$$= 3130 \text{ l mole}^{-1} \text{ cm}^{-1}$$

Sandell Sensitivity

$$S = 10^3 \times A \times C \text{ min where } C \text{ min} = \frac{Dmin}{Exb}$$

A = Atomic wt.

$$= 10^3 \times 96 \times \frac{0.001}{3.130 \times 10^3 \times 1}$$

$$= 31 \text{ ng/cm}^2$$

Effect of diverse Ions :

Various cations and the anions as indicated in the Table-3 were tested for interference in the determination of 0.4 mg of Mo(V) using 4.8×10^{-3} M reagent at 3 M HCl concentration. An error of less than 2 percent in absorbance was considered to be tolerable. The samples were prepared as outlined in the general procedure. The absorbance was measured at 510 nm against reagent blank.

The tolerance for various foreign ions tested has been shown in Table-3. It was observed that the cations which didnot interfere when present in 10 fold excess relative to Mo were Ni(II), K(I), Ba(II), Co(III), V(V), Zn(II), Al(III), Ca(II), Li(I), Na(I), Mg(II), Mn(II) As(III), Sb(III). The cations which are tolerable in 1:1 ratio were Rh(III), Pt(IV), Ir(III) and Os(III). Only ions showing interference were Bi(III), Tl (III), Fe(III), Cu(II), W(VI), Cd(II), Pb(II), Hg(II), Se(IV), U(VI), Te(IV), Au(III), thiosulphate, ascorbic acid and $NaNO_2$. Relatively large amount of anions could be tolerated in the determination of 0.4 mg of Mo(V)

Table 3 : Effect of Diverse Ions
Mo(V) = 0.4 mg; Aqueous phase = 3M HCl
5 Methyl SAT = 25 mg in alcohol; λ max = 510 nm

Foreign ion	Tolerance limit in mg
Ni (II)	5
k (I)	5
Ba(II)	5
Co (III)	5
Bi (III)	Interfere
Tl(III)	Interfere
Fe(III)	Interfere
Cu(II)	Interfere
V(V)	5
Zn(II)	5
W(VI)	Interfere
Cd(II)	Interfere
Pb(II)	Interfere
Al(III)	5
Ca(II)	5
Li(I)	5
Na(I)	5
Mg(II)	5
Hg(II)	Interfere
Mn(II)	5
Se(IV)	Interfere
U (VI)	Interfere
Rh(III)	0.5

1	2
Pt (IV)	0.5
Ir(VI)	0.5
Te(IV)	Interfere
Au(III)	Interfere
Os(VIII)	1
As(III)	5
Sb(III)	5
Acetate	100 mg
Thiocynate	100 mg
Thiosulphate	Interfere
Citrate	100 mg
EDTA	100 mg
Oxalate	100 mg

Application

The proposed method has been successfully applied for the determination of molybdenum in steel sample 31b and 33 d A known weight (31b, 2.5 g or 33d 2g) of sample of alloy cast iron BAS Ltd. was dissolved in 10 ml of hydrochloric acid (1:1)with mild heating. A few drops of conc. HNO_3(1 ml) were added carefully. The resulting solution was evaporated to incipient dryness. The residue was dissolved in 10 ml of 0.5 N HCl. The iron (III)was then extracted by shaking for one min with successive 10 ml portions of 1:1 volume ratio of acetylacetone and chloroform until iron was removed (traces of iron do not interfere in the determination of Mo). Theaqueous phase after removal of iron was made to 100 ml in volumetric flask with distilled water. In case of sample 33d the pH of the aqueous phase after removal of iron(III) was increased to 2.5 and copper was then removed by repeating extractions with a mixture of acetylacetone and chloroform.

A suitable aliquot of this diluted solution was taken and the colour of the complex was developed as per the recommended procedure and measured at 510 nm against water. The results of analysis are summerised in Table-4. Each result is the average of four determinations. The results are accurate to within $\pm$ 2 %.

Table -4 : Application of Steel Analysis

Sample	Reported value M_o (%)	This work M_o (%)
Alloy cast iron (BAS 33b) Composition C 2.24, Si2, P 0.11, Mn 0.64, Ni 2.24, Cr 0.6	0.40	0.40
Alloy cast iron (BAS 33d) Composition C 2.3, Si 1.63, Mn 0.63 Ni 2.38, Cr 0.52, Cu 1.54	0.48	0.49

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