C H A P T E R - V

**PHOTOMETRIC DETERMINATION OF CHROMIUM (III)
WITH 2CHLOROQUINOLINE 3 - CARBALDEHYDE
THIOSEMICARBAZONE**

INTRODUCTION

In 1762, J.G. Legmann described a new mineral from Siberia. We now know this mineral to be crocoisite, or lead chromate. Both L.N. Vauquelin and Macquart, in 1789, failed to recognise in the mineral a new element and both reported lead, iron, alumina and a large amount of oxygen. However, in 1797, L.N. Vauquelin, reexamined the mineral and concluded that lead must be combined with a peculiar acid which he considered to be the oxide of a new metal. This is called 'chromium', from the Greek word (CHROMA), colour - because its compounds are all coloured. In 1798, L.N. Vauquelin detected the new element in spinel and in smaragdite, and F. Tassert found chromium in chrome iron ore in 1799.

Metallic chromium does not occure free in nature. It occurs combined with oxygen in chromium sequioxide, Cr_2O_3, associated with more or less earthy matters. It also occures as lead chromate in crocoisite, $PbCrO_4$. Traces occur in many minerals - emerald, jade, serpentine etc.

The principle source of chromium is chrome iron ore (chromite). Metallic chromium is made commercially by the 'thermite' process and by reduction of chromic oxide by

means of the theoretical amount of silicon in an electric arc furnace.

Chromium is one of the more satisfactory elements from the standpoint of colorimetric trace analysis. It can be determined very sensitively and can also be separated fairly easily from other elements.

Chromium is present in the air-borne dust, atmospheric aerosols[1], in biological material such as tissue, blood. It is also present in urine[2], brovine liver[3].

Chromium is also present and can be determined from the nickel alloys, Zirconium alloys, steel[4], Silicates, ores or rocks[5], magnesium oxide[6], gallium arsenide[7], copper alloys[8], cemented carbides[9], cadmium mercury telluride[10], petrolium or petrolium products, in tin[11] and in muncipal sediments and sea water etc.

The most useful method for the separation of chromium involves oxidation in basic medium, where by chromate is formed and remains in solution while a great many metals such as iron, titanium, manganese, nickel and cobalt are precipitated.

Thus chromium can be determined by various techniques such as the atomic absorption spectrophotometry, emission spectrophotometry, spectrography etc.

5.1 Review of the methods for Photometric determination of Chromium

Reagent	pH	λmax.	Molar extinction coefficient, sandell sensitivity, Bear's Law, ppm.	Interference	Reference
1	2	3	4	5	6
EDTA	5.3 to 6	550	Beer's law obeyed for 1 to 15 μg of Cr in 50 ml soln.	-	21
Alizarin red S	3 to 8	525 mμ	Beer's law obeyed by 0.2 to 10.4 ppm of Cr. Sandell sensitivity is 0.52 μg.	-	22
Catechol violet	5.4	590	{Cu(II), Zn(II), Mn(II)} - interfere but not interfered by Cl^- NO_3^-, SO_4^{2-}, F^-.}	-	23
Mercaptoacetic acid	7 to 10	632	Beer's law is obeyed with 20-150 μg of Cr.	Fe, V and U interfere.	24
3-hydroxy-4-naphthlene 1-sulphonic acid	10	630	Sandell sensitivity is 0.0013 μg of Cr. Beer's law is obeyed upto 1.2 ppm of Cr.	Intereference by Al, Fe(III), Be, Sc, Ca while Cr(VI), Cl^- and SO_4^{2-} do not interfere.	25
EDTA	4.5	545	ϵ = 154.5	-	26

1	2	3	4	5	6
Xylenol orange	2	527	-	Interference due to Nitrilotriacetic acid, EDTA.	27
Methyl thymol blue	-	560	$\varepsilon = 11.5 \times 10^3$	-	28
Xylenol orange	-	530	$\varepsilon = 19 \times 10^3$	-	29
8-aminoquinoline	2.4 to 2.8	550	-	-	30
Catechol violet	-	605	-	V, Ni, Mo do not interfere.	31
azorubine (C.I.Acid Red 14).	-	620	-	Fe(III), Vo_3^- interefere.	32
Xylenol orange	3-6	550	Beer's law is obeyed for 0.06 to 5.2 μg of Cr per ml.	-	33
3-thianaphthenoyl-trifluoroacetone.	4-4.5	460	$\varepsilon=1300$	-	34
EDTA (disodium salt)	4.5	390 and 450	Beer's law is obeyed with 5 to 150 μg Cr per ml.	-	35
8-Mercaptoquinoline	3.5 to 5.5	450	$\varepsilon=12,400$ Beer's law is obeyed for 0.1 to 6 μg of Cr(III) per ml.	Ag,Au,Mn,Zn, do not interfere.	36
(1,2-diamino-cyclohexa-N-NN'N'-tetra acetic acid)	3.7-4.5	540	-	Beer's law is obeyed for upto 650 μg of Cr. Co, Ni interfere.	37
EDTA	3-3.5	546	-	-	38

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1	2	3	4	5	6
diphenyl carbazide (in acetone)	—	542	$\varepsilon = 43{,}000$	—	39
Helasol violet 4R	—	580	—	Al, Pb, Zn, Ag does not interfere while Hg(II), Pt, Cu interfere.	40
O-hydroxyquinolphthalein and hexadecyl trimethyl ammonium chloride.	5.8	560	$\varepsilon = 164{,}000$ Sandell sensitivity to 0.32 ng Cm^{-2}	—	41
1,2-diaminopropane-N,N,N'N' tetra acetic acid.	—	540	—	—	42
4-(2-pyridylazo) resorcinol.	3.5	540 to 545 nm	$\varepsilon = 29{,}870$ Beer's law is obeyed for 0.08 to 1.5 µg/ml. Sandell sensitivity is 1.8 ng Cm^{-2}	—	43
Glycinethymol blue	6.5 to 7.0	570	Sandell sensitivity is 0.00236 mg Cm^{-2} Beer's law is obeyed for 26 to 136 µg of Cr. in 25 ml.	—	44

1	2	3	4	5	6
arsenazo(III)	2.5	580	ε = 26,000	Co, Ni, Zn and Cd do not interfere.	45
Thoron	2.5	500	ε = 7000	Zr, Ga, No_2^- interfere.	46
P-anisidine	3	405	-	-	47
dpta (diethylene triamine-N,N,N'N"N"' - penta-acetic acid).	-	555	-	-	48
4-(2-thiazolyazo) resorcinol.	5	525	Beer's law is obeyed for 0.06 to 1.1 μg per ml.	-	49
Ammonium-pyrrolidine-1-carbidithioate.	-	265	-	Na, Mg, Al, K, Ca can be tolerated but Cu, Fe(II), Fe(III) and Co interfere.	50
Uramil diacetic acid	3.5-4.8	420	Optimum range 500 to 1500 μg per ml.	As(V) and W(VI) interfere.	51
3-hydroxy-4-(2-hydroxy-sulpho-1-naphthylazo)-naphthalene-2, 7-disul-phonic acid.	10	650	Limits of detection in the range 0.026 to 0.16 μm.	-	52
1,2-diaminocyclohexane tetraacetic acid.	-	395 or 555.	Optimum analytical range 20 to 167 μg per ml.	Fe(III), Co, interfere.	53

1	2	3	4			5	6
4-(2-pyridylazo) resorcinol.	—	530	$\mathcal{E} = 51,000$			—	54
2-pyridylmethanamine				$\mathcal{E}$		—	55
			CrL	CrL_2	CrL_3		
		350	73	650	383		
		400	43	759	109		
		500	33	403	148		
		600	22	253	141		
		700	0.02	187	126		
Sodium Iodide (in .012 M $HClO_4$)	—	354	Sandell sensitivity is 1 ng Cm^{-2}. Optimum analytical range is 0.17 to 1.31 µg per ml.			—	56
Calcon	10	635	Beer's law obeyed for 0.5 to 30 µg per ml.			—	57
Calcon and alloxan	—	610	—			Co, Mn(II), Zn do not interfere.	58
2', 3', 4' - trihydroxyaceto-phenone oxime	—	410	$\mathcal{E} = 3600$. Sandell sensitivity is 0.015 µg Cm^{-2}. Beer's law obeyed for 2 to 16 ppm of Cr.			—	59

1	2	3	4	5	6
Eriochrome Cyanine R and hexadecyltrimethyl ammonium bromide.	5.5 to 6	590	$\varepsilon = 78{,}000$ Beer's law is obeyed for upto 14 μg of Cr. in 25 ml.	No interference of W or Mo but Al, Cu, V, Fe, Co, Ni interfere.	60
Ferrozine	3 to 3.5	562	Satisfactory results for solution containing Cr(III).	MnO_4^- interferes.	61
bis-(2,4-diaminophenyl) phosphate.	3-4.5	465	$\varepsilon = 6500$ Sandell sensitivity is 7.47 ng Cm^{-2}.		62
		500	$\varepsilon = 3850$ Sandell sensitivity is 13.4 ng Cm^{-2} Beer's law is obeyed for 20 to 100 μg of Cr in 50 ml.	SO_3^{2-}, Cu(II) and Fe(III) interfere.	
{4-(1-(2-amminophenyl-imino) ethyl)resorcinol}	-	490	$\varepsilon = 6900$ Optimum range is 1.5 to 5.2 μg per ml. Beer's law obeyed with 0.3 to 6.8 μg per ml of Cr.	F^-, SCN^-, Ca, Ba, Ni, Zn do not interfere.	63
Azure B - EDTA	4.5	530	-	Co and large amounts of Fe(III), Cu(II) and Ni interfere.	64

1	2	3	4	5	6
2-(5-bromo-2-pyridylazo)-5-dimethylaminophenol.	-	600	Beer's law obeyed in the range 0 to 15 μg Cr in 25 ml.	Fe(III), Cu(II), Co, Ni,Zn-Ti(III) interfere.	65
Iodine-EDTA	4 to 5	540	Optimum range in 10 to 170 ppm.	Fe, Co, Ni do not interfere.	66
Phenylfluorone (2,6,7-trihydroxyxanthen-3-one).	1 to 5	490	Beer's law obeyed in the range 13 to 1700 ppb of Cr.	$W(VI)$ and MnO_4^- interfere but Ag, Be, Au(III), Fe(II) do not interfere.	67
3',4'-Dicarboxyarsenazo 4-(7-(2-arsonaphenylazo)-1,8-dihydroxy-3,6-disulpho-2-naphthylazo) phthalic acid.	2.2	625	$E = 47,000$ Beer's law obeyed for upto 1 μg per ml of Cr.	-	68

Chromium is an element which gives sensitive and satisfactory colour reactions with innumerable organic reagents. Many colorimetric reagents have been prepared for the determination of chromium. Some of them are 2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol[12], 3',4'-dicarboxyarsenazo[13], diphenyl carbazide[14], MEDSHA[15], phenylfluorone[16], tetrophenyl arsonium chloride[17].

Chromium can be separated from the alloys. The separation of chromium can be done by the precipitation methods, extraction methods, chromatographic methods.

Chromium can be separated from other elements such as Fe, Co, Mn, Mo, Ni by HPLC of dithiocarbate complexes[18,19] and with Macrocyclic compounds[20].

The detailed summary of reported photometric methods for chromium determination is given in table 5.1.

The present work accounts for spectrophotometric determination of Cr(III) by 2-chloroquinoline-3-carboldehyde thiosemicarbazone (QAT). Chromium (III) forms complex with 2-chloroquinoline-3-carbaldehyde thiosemicarbazone (QAT). For chromium optimum pH is 9.5 and λ max is 460 nm. Beer's law is obeyed upto 4 ppm of Chromium (III). The effect of pH, reagent concentration and diverse ions have

been studied. The molar absorptivity and sandell sensitivity are 1.976×10^4 L mole^{-1} cm^{-1} and 0.042 ng cm^{-2} respectively at 460 nm. The dissociation constant of complex Cr (III) - QAT is 1.038×10^{-4}. For Cr (III), Fe, V, Ni, Co interfere.

EXPERIMENTAL

1. Standard Chromium Solution :

Standard chromium solution 1 mg/ml was prepared from Chromic Potassium Sulphate and the solution was standardised with EDTA volumetrically[69]. Further dilution for experimental purposes were made by diluting the stock solution with distilled water.

2. Reagent Solution :

.052 gm QAT was dissolved in DMF and diluted to 100 ml. The molarity of the solution is 1.96×10^{-4} M. The solution is found to be stable for more than a weak.

Recommended Procedure :

To an aliquot of solution containing upto 2 ppm of chromium, add 1 ml of 1.96×10^4 M reagent solution and a buffer solution of pH 9.5. Dilute this to 10 ml with DMF

water (3:2) in a volumetric flask. Measure the absorbance against reagent blank.

RESULT AND DISCUSSION

Spectral Characterisatics :

Figure 5.1 shows the absorption spectrum of the chromium (III)-QAT Complex containing 1.923×10^{-5} M of chromium and 1.96×10^{-4} M reagent at pH 9.5 using reagent blank. Absorption measurements were made in the spectral region 400 nm to 650 nm and recorded in the table 5.2. From the graph it was found that 460 nm will be suitable wavelength for chromium determination. The molar absorptivity of the complex is 1.976×10^{4} at 460 nm.

Table 5.2 : Molar Extinction Coefficients of
Cr(III)-QAT Complex

$QAT = 1.96 \times 10^{-4}$ M, $Cr(III) = 1.923 \times 10^{-5}$ M,
pH = 9.5

λ nm	Molar Ext. Coefficients of the complex x 10^4 L mole^{-1}cm^{-1}
400	.3900
410	.8060
420	1.222
430	1.430

λ nm	Molar Ext. Coefficients of the complex x 10^4 L mole^{-1}cm^{-1}
440	1.690
450	1.846
460	1.976
470	1.976
480	1.872
490	1.638
500	1.378
510	1.091
520	0.832
530	0.598
540	0.416
550	0.286
560	0.104
570	0.078
580	0.052
590	0.028
600	0.026
610	0.020
620	0.015
630	0.008
640	0.008
650	0.008

FIG. 5·1 — ABSORPTION SPECTRUM OF
Cr(III) — QAT COMPLEX .

Effect of Time :

In order to study the effect of time on the absorbance of chromium - (III)-QAT complex containing 1.923 x 10^{-4} M Cr (III) -QAT at pH 9.5, the absorbance measurements were recorded at different time intervals at 460 nm. It was observed that the complex is stable for 24 hours.

Effect of Reagent Concentration :

Solutions containing the same amount of Chromium (1.923 x 10^{-4} M) but different amounts of reagent varying from 0.1 to 1 ml of 1.96 x 10^{-4} M reagent solutions were prepared. The pH 9 buffer was added and the solution was made upto 10 ml with DMF : water (3:2). Absorbance measurements were recorded at 460 nm against simultaneously prepared reagentblank. The data given in the table 5.3, Fig. 5.2 shows that 1.923 x 10^{-4}M chromium solution required minimum 1 ml of 1.96 x 10^{-4} M reagent solution for maximum complexation. At higher concentration of the reagent there was insignificant increase in absorbance. However, 1 ml of 1.96 x 10^{-4} M reagent solution was employed to ensure maximum colour intensity of the chromium complex.

Table 5.3 : Effect of Reagent Concentration on
the absorbance of Cr-QAT Complex

Chromium (III) = 1.923×10^{-4} M, pH = 9.5

QAT = 1.96×10^{-4} M

Reagent ml	Absorbance at 460 nm
.2	.05
.4	.13
.6	.22
.8	.30
.9	.34
1.0	.35
1.2	.355

Effect of pH :

A series of solutions containing 1.923×10^{-4} M
Cr(III) and the same amount of 1.96×10^{-4} M reagent but
varying in pH from 2 to 12 were prepared and the
absorption measurements were recorded at 460 nm. The
results are summarised in the table 5.4. It was observed
that maximum absorbance was obtained at the pH 9.5. The
absorbance of the solution decreased at higher or lower
pH values than this, which is shown in figure 5.3. Hence
pH 9.5 was maintained in further studies.

Table 5.4 : Effect of pH on the absorbance of
Cr-QAT Complex

$Cr(III) = 1.923 \times 10^{-4}M$, $QAT = 1.96 \times 10^{-4}$ M

pH	Absorbance at 460 nm
5	.10
6	.16
7	.22
8	.29
9	.35
9.5	.38
10	.34
11	.27

Validity of Beer's Law and Sensitivity :

The solutions (final volume 10 ml) containing different amounts of Chromium and the same amount of reagent (1.96×10^{-4} M) with the pH maintained at 9.5 were used for the study. The absorption measurements were recorded against reagent blank at 460 nm (Table 5.5, Fig.5.4). Beer's Law is obeyed upto a concentration of 4 ppm of Chromium (III). The Sandell sensitivity[70] of the reaction is .042 Mg cm^{-2} of Cr (III) at 460 nm. The Ringbom's plot (Fig. 5.5) indicates that the optimum range is 3 to 5 ppm of Chromium (III).

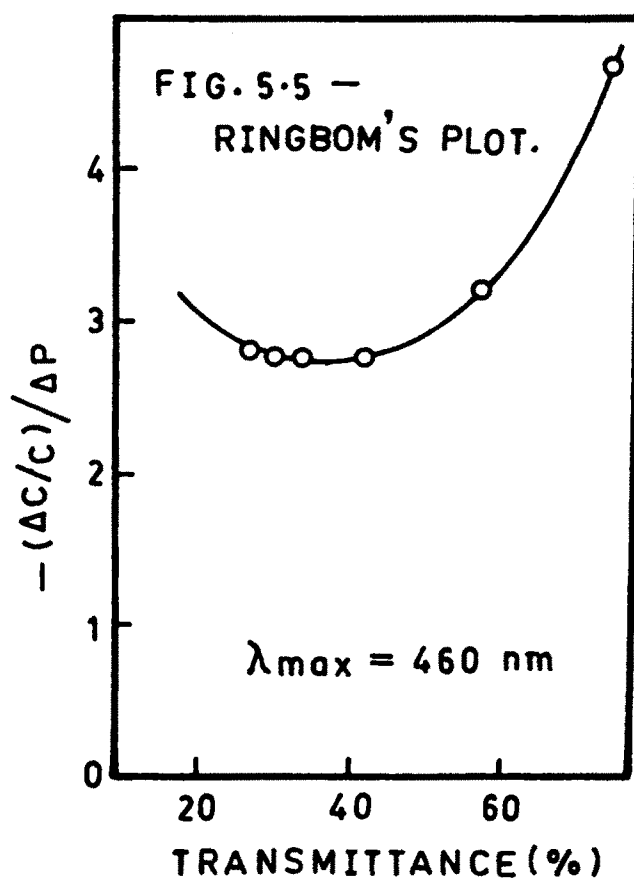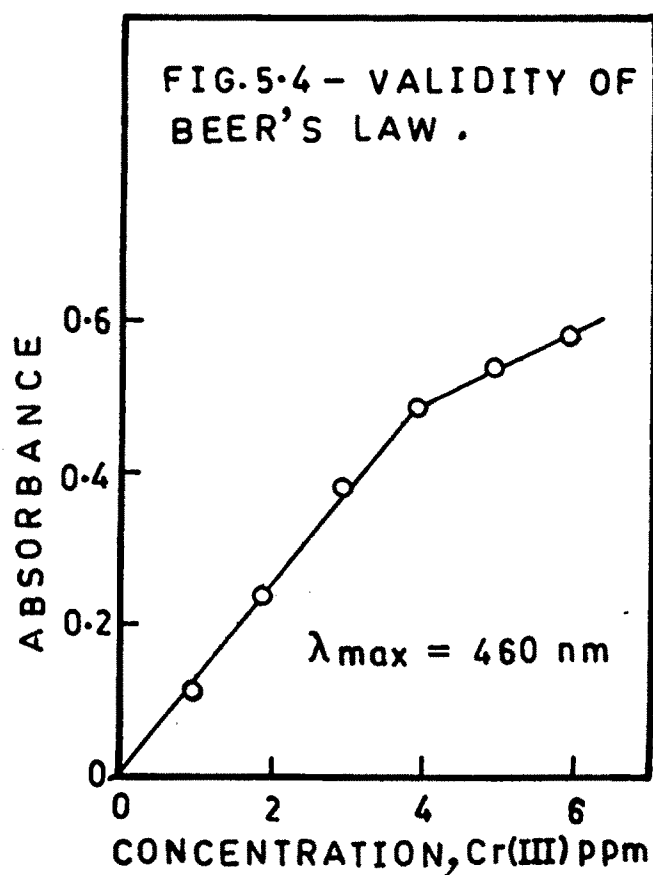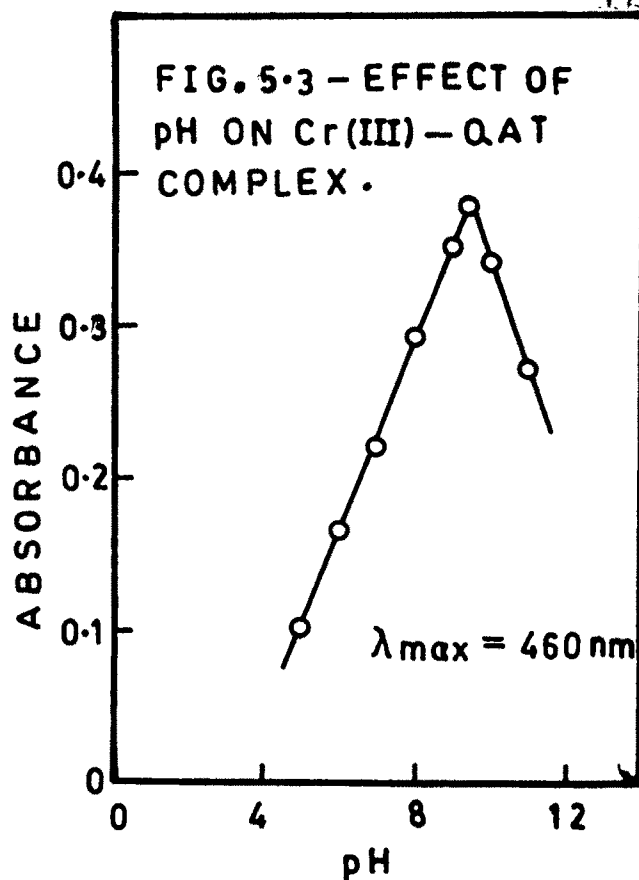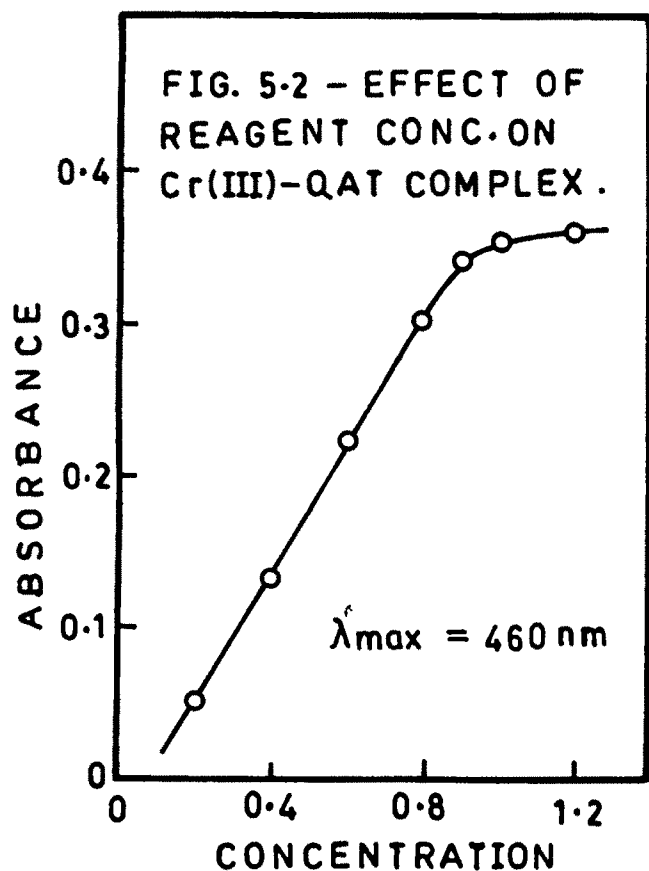FIG. 5·2 – EFFECT OF REAGENT CONC. ON Cr(III)–QAT COMPLEX.

λmax = 460 nm

FIG. 5·3 – EFFECT OF pH ON Cr(III)–QAT COMPLEX.

λmax = 460 nm

FIG. 5·4 – VALIDITY OF BEER'S LAW.

λmax = 460 nm

FIG. 5·5 – RINGBOM'S PLOT.

λmax = 460 nm

Table 5.5 : Verification of validity of Beer's
Law for Cr-QAT Complex

$$QAT = 1.96 \times 10^{-4}M \ , \ pH = 9.5$$

Cr(III) taken ppm	Absorbance at 460 nm
1	.120
2	.240
3	.380
4	.460
5	.520
6	.560

Composition of the Complex :

The combining ratio of metal to reagent was ascertained by Job's method of continuous variation[71] and Mole Ratio method.[72] For Job's method of continuous variation, a series of solutions were prepared by mixing equimolar solutions of the Chromium (III) and the reagent ($1.96 \times 10^{-4}M$). The pH of the solution was adjusted to 9.5. The absorbances of the solution after diluting to 10 ml in volumetric flask were recorded at 460 nm against simultaneously prepared reagent blank (Table 5.6,Fig.5.6).

The plot indicate the existance of 1:3 complex with respect to metal and reagent represented as ML_3 .

Table 5.6 : Determination of the formula of the Cr-QAT Complex by Job's method of continuous variation

$Cr(III) = QAT = 1.96 \times 10^{-4}$, pH = 9.5

Metal ion ml	Reagent ml	Mole fraction of metal	Absorbance at 460 nm
.1	.9	.1	.09
.2	.8	.2	.15
.25	.75	.25	.17
.3	.7	.3	.16
.4	.6	.4	.135
.5	.5	.5	.11
.6	.4	.6	.09
.7	.3	.7	.08
.8	.2	.8	.05
.9	.1	.9	.04

Mole Ratio Method :

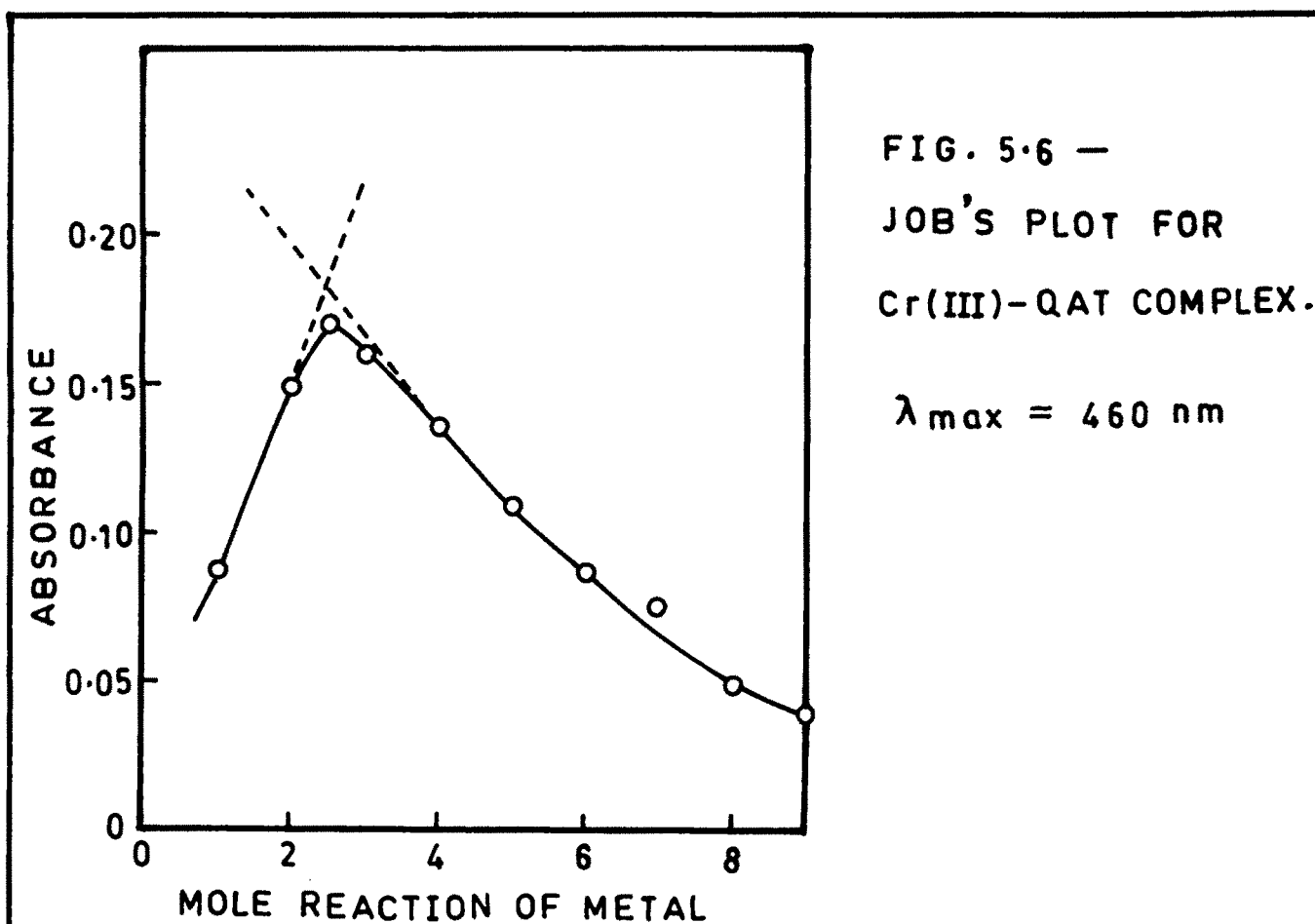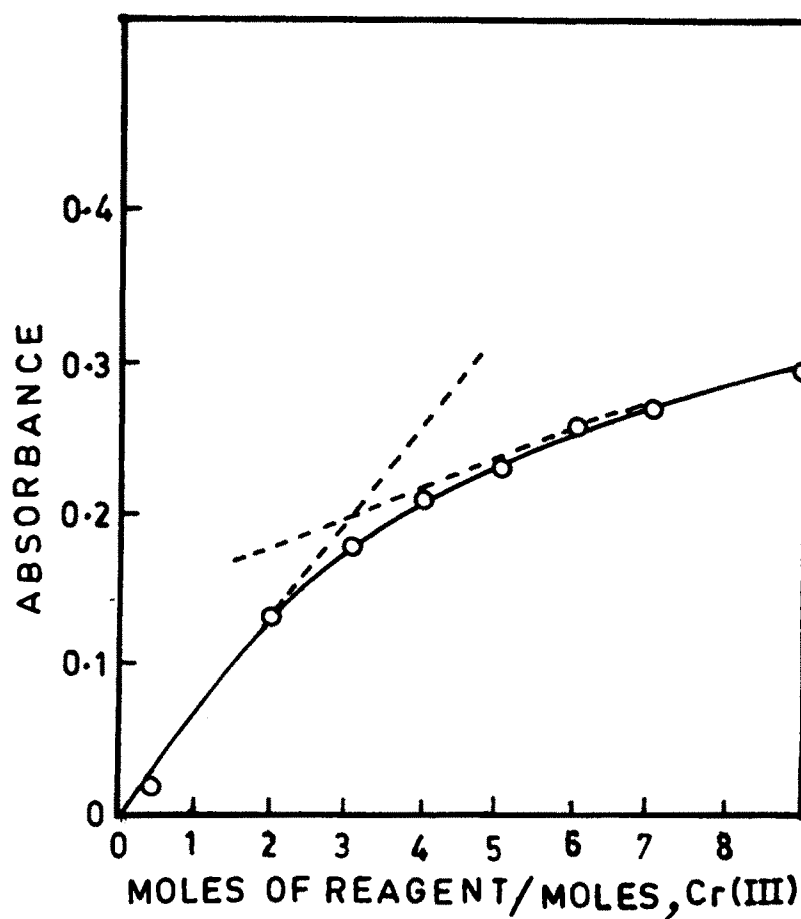For mole ratio method, solutions containing the same final metal concentration and different amounts of reagent

FIG. 5·6 —
JOB'S PLOT FOR
Cr(III)—QAT COMPLEX.

$\lambda_{max} = 460$ nm

FIG. 5·7 —
MOLE RATIO PLOT
FOR Cr(III)—QAT
COMPLEX ·

$\lambda_{max} = 460$ nm

were prepared keeping pH 9.5. Absorbances of the solutions were measured at 460 nm against reagent blank. The curve showed break at the metal ligand ratio 1:3, confirming the results obtained by application of Job's method of continuous variation (Table 5.7, Fig.5.7). The dissociation constant is calculated from mole ratio plot and comes out to be 1.038×10^{-4}.

Table 5.7 : Determination of the formula of the
Cr - QAT Complex by Mole Ratio Method

$$Cr = 1.96 \times 10^{-4}M, \quad QAT = 1.96 \times 10^{-4}M, \quad pH=9.5$$

Metal ion ml	Reagent ml	Reagent to metal ratio	Absorbance at 460 nm
.4	.8	2	.06
.4	1.0	2.5	.13
.4	1.2	3.0	.18
.4	1.4	3.5	.21
.4	1.6	4.0	.23
.4	1.8	4.5	.26
.4	2.0	5.0	.27
.4	2.4	6.0	.29

Effect of diverse ions :

The effect of diverse ions was studied using 2 ppm of $Cr(III)$ and 1.96×10^{-4} M reagent in a final volume of 10 ml at pH 9.5. The results indicated that Phosphate, Citrate, Fluoride interfere. The tolerance limit for various ions tested has been shown in the table.

Effect of diverse ions :

$Cr(III) = 2$ ppm, $QAT = 1.96 \times 10^{-4}$M; pH=9.5

Metal ion	Tolerance limit μg
Na^{+}	50
$Ca(II)$	50
$Ba(II)$	50
$Cd(II)$	50
$Zn(II)$	50
$Ni(II)$	20
$Al(III)$	20
$Cu(II)$	5
$Mn(II)$	5
$Co(II)$	5
Nitrate	None
Sulphate	None
acetate	None
tartrate	None

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