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## CHAPTER - I V

PHOTOMETRIC DETERMINATION OF IRON (III) WITH  
6-METHYL 2-CHLORO QUINOLINE 3-CARBALDEHYDE  
THIOSEMICARBAZONE

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## INTRODUCTION :

Iron was detected by 2', 4', Dihydroxy acetophenone ethylenediamine ( $\alpha\alpha'$ -ethyl-ehedi-imino) bis-(4-ethylresorcinol) as indicator for direct EDTA titrations<sup>1</sup>. Iron in imcroamounts determined by spectrophotometric complexometric titrations<sup>2</sup>.

Titrimetric determination of iron was done using Cacotheline as indicator<sup>13</sup>.

Flow injection methods was usual for determination of Iron<sup>14</sup>(III).

Iron (III) after seperation by adsorption of its 5-Chloro-7-iodoquinolin-8-0 - complex on microcrystalline Naphthalene<sup>3</sup>. Iron (III) with thiocynate in the presence of Triton X-100<sup>4</sup> was determined (and its application to the analysis of lime stone aluminium or water).

Reaction of iron (II) and iron (III) was done with certain pyrlldylazo-compounds and their halogen derivatives<sup>5</sup>. Evaluation of sample moulds for chemical analysis of cast iron was done by vacuum emission spectrometry<sup>10</sup>.

Some observations on determination of iron were done by atomic absorption spectrophotometry using air acetylene flames<sup>19</sup>. Precise determination of iron in iron ore was carried out by controlled-potential culometry<sup>20</sup>.

Improved method were observed for detecting microgram amounts of iron<sup>26</sup>. Determination of iron (II) and iron (III) was done by flow injection and amperometric detection with a glassy carbon electrode<sup>27</sup>.

Indirect polarographic determination of microgram amounts of iron was done by means of the catalytic oxidation of 5-amino salicylic acid<sup>6</sup>.

Chemical characterisation of hydrous ferric oxides was done by X-ray photoelectron spectroscopy<sup>7</sup>. Determination of the principal substance in technical grade iron (II) bromide<sup>8</sup>. Determination of chloride in technical grade iron (II) bromide<sup>9</sup> and X-ray fluorescence study of composition of high alloy steels and high chromium cast iron and steel<sup>17</sup>. were done.

Rapid photometric determination was done of aluminium in iron and steel<sup>11</sup>. Qualitative and semi-quantitative determination of iron (III) was done in aqueous thiocyanate solution using tricaprylylamine foam<sup>12</sup>.

3-Aldehydosalicylidene cyanoacetyl hydrazone as a new reagent for the spectrophotometric determination was done of ferric ions<sup>18</sup>.

Spectrophotometric study of 3-hydroxy picolinaldoxime and its reaction with iron<sup>24</sup>. Spectrophotometric determination of Ultratrace amounts of iron by its catalytic effect<sup>25</sup>,

Study of iron (III) and gold (III) separation by paper chromatography using di-isopropyl ether<sup>15</sup>, analysis is of ferric chloride) etching solution were done for intaglio printing plates<sup>16</sup>.

Coulometric titration of iron and Vanadium when present together<sup>26</sup>, complexation reactions of hydroxy coumarins, reaction of iron with 3-hydroxy coumarin<sup>22</sup>. Ultra-violet spectrophotometric determination of iron with 2-thenyltrifluoroacetone in an aqueous solution were done containing  $\alpha$ -hydro- $\omega$ -dodecyloxynona<sup>23</sup>.

Iron has industrial importance which exceeds that of any other element. It is a key element in industries and plays a vital role in Science, technology, metallurgy and also plays an important role in the functioning of red Corpuscles of blood (haemoglobin) and of the respiratory, ferment porphyrins and also of plant tissues. The analytical chemists are concerned with iron in the samples ranging from food materials, medicinal preparations, ores and minerals, metals and alloys, blood and other body fluids etc.

Numerous colorimetric reagents are reported for tracer determination of iron. Phenolic compounds give purple or violet coloured complexes with iron (III). In the case of reagents like  $\alpha$ -pyridyl hydrazone<sup>28</sup>, Pyridil- $\beta$ -monoxime<sup>29</sup>, glycine cresol red<sup>30</sup>, and 2-benzoyl pyridine hydrazone<sup>31</sup>, heating is necessary due to slow rate of formation of the

complex. Reagent like O-dianisidine<sup>32</sup>, 2-pyridyl glyoxime<sup>33</sup>, formaldoxime<sup>34</sup>, dimethyl triketone<sup>35</sup> catechol<sup>36</sup>, quinisatin oxime<sup>37</sup>. Colour formation is very slow and requires longer duration of time. Methods involving 2thenoyl trifluoroacetone<sup>38</sup>, dinitroso-resorcinol<sup>39</sup>, phenyl 2-pyridyl ketoxime<sup>40</sup>, O-hydroxy acetophenone oxime<sup>41</sup>, and chromotope 2R<sup>42</sup>, as reagents are not selective where sensitivity of the methods is very low in case of O-hydroxy acetophenone oxime<sup>41</sup> and chromotope 2R<sup>42</sup>. Among the other reagent that have been used for photometric determination of iron, the following may be mentioned; pyramidone<sup>43</sup>. Salicylaldoxime<sup>44</sup>, Cuferron<sup>45</sup> Rhodamine B<sup>46</sup>, 2-formyl pyridine-2 hydroxy benzoyl hydrazone<sup>47</sup> Bis (2-9-dimethyl 1-1- 10 phenanthroline<sup>48</sup>), Thiodi-benzoyl methane<sup>49</sup> Di-2 pyridyl ketone azine<sup>50</sup>, di(2-pyridyl) ketone-2-furoyl hydrazone<sup>51</sup> Brilliant cresyl blue<sup>52</sup>, 2,2' Dipyridyl-2- quinolyl hydrazone<sup>53</sup>, phenathraquinone monoxime<sup>54</sup>, - furil dioxime<sup>55</sup>, 2-2'-Dipyridyl -ketoxime<sup>56</sup> Erich-rome cyanine<sup>57</sup> 1-Phenyl -3-quinolyl-2-thiourea<sup>58</sup>. Syn-phenyl-2-pyridyl ketoxime<sup>59</sup> complexes of p-amino-NH-dimethyl aniline<sup>60</sup>, 5-Sulpho- $\beta$ -resorcylic acid<sup>61</sup>, 8-hydroxy-7-nitro-quinoline-5-sulphonic acid<sup>62</sup>, are stable for atleast 10-20 minutes. Reagents such as 2 formyl pyridine azine<sup>63</sup> 2- (5-bromo-2-pyridylazo)-5-diethyl aminophenol<sup>64</sup>, 2'-hydroxyl-5'-methyl pripiophenone oxime<sup>65</sup>, 1(2-quinolylazo)-2,4,5-trihydroxy benzene<sup>66</sup>, are reported for determination of iron.

Recently for trace determination of iron, some thiosemicarbazones are reported. But most of them are affected by one or the other drawback discussed earlier. Such are Biacetyl monoxime 4-phenyl-3-thiosemicarbazone<sup>67</sup>, 2-Benzo pyridine-4-phenyl-3-thiosemicarbazone<sup>68</sup>, 2'-hydroxy-5'-methyl acetophenone thiosemicarbazone<sup>69</sup>, salicylaldehyde thiosemicarbazone<sup>70</sup>, Di-2-pyridyl ketone thiosemicarbazone<sup>71</sup>, 2-Acetyl-pyridine 4-phenyl-3-thiosemicarbazone<sup>72</sup>, Quinoline-2-aldehyde thiosemicarbazone<sup>73</sup>, Bipyridyl glyoxal dithiosemicarbazone<sup>74</sup>.

The present work accounts for the spectrophotometric determination of iron (III) by 6-Methyl-2-chloroquinoline 3-Carbaldehyde thiosemicarbazone (6-Me-QAT). Iron forms yellow coloured complex with 6-Me-QAT at pH-5. Beer's law is obeyed upto 5 ppm of iron(III) at 380 nm. The effect of pH, reagent concentration and diverse ion have been studied. The dissociation constant of the complex is  $6.092 \times 10^{-4}$ .

The molar absorptivity and Sandell sensitivity are  $2.548 \times 10^4 \text{ l Mole}^{-1} \text{ cm}^{-1}$  and  $0.016 \mu\text{g cm}^{-2}$  respectively. Cations like zinc, palladium interfere seriously like Zinc, palladium interfere seriously while Pb(II), Mn(II), Ni(II) tolerated at tracer concentration. Anions like EDTA, Chloride, Oxalate do not interfere but fluoride and tartrate interfere in the determination of iron (III).

Table 4.1 : Reviews of the methods for Photometric Determination of Iron (III)

Reagent	pH	max	Sensitivity, molar extinction Coefficient range ppm	Interference and remarks	Ref.
1	2	3	4	5	6
2-thenoyl trifluoro acetone	pH 1.0	500	$\epsilon = 4600$	$\text{SO}_4^{2-}$ , $\text{NO}_3^-$ , Cu, MO, W, Co(II), interfere	38
Phenyl-2-pyridyl ketoxime	4.5 to 5.0	596	-	Aqueous solution should be heated.	39
O-Hydroxy aceto-	3.7 to 8.5	420	Sensitivity is 0.013 <del>mg</del> $\text{cm}^{-2}$	Na, K, $\text{NH}_4^+$ , $\text{Cl}^-$ , $\text{I}^-$ , $\text{NO}_3^-$ do not interfere	40
Phodamine B	4.3 to 5.3	558	$\epsilon = 9 \times 10^4$	Determined in water	41
2-Formyl pyridine 2-Hydroxy benzoyl hydrazone	4.0 to 4.7	640	$\epsilon = 0.3 \times 10^4$	-	42
Bis-(2-g-dimethyl-10-phenanthroline)	4.5 to 5.0	596	-	Fe determined in sea water and tap water	43

1	2	3	4	5	6
Thiodibenzoyl methane	6.5	480	-	Cu(II), Co(II) Zn, Ni Cd, EDTA interfere	44
Di-2-pyridyl ketone azine	6.5 to 7.5	460	$C = 9.299 \times 10^3$	Ni(II), Bi(III), Sb(III) Au(II) tartrate interfere	45
Di(2-pyridyl) ketone 2-formyl hydrazone	5.3 to 11.3	620	$C = 8.4 \text{ to } 10^3$	Determination of iron in cement.	46
Brilliant cresyl blue	4.0 to 6.0	630	$C = 24600$	Ga, Bi(III), Au, Tl(III) interfere	47
2,2'-Dipyridyl -2-quinolyl hydrazone	3.4 to 4.5	605	$3.11 \times 10^4$	--	48
Phenanthra- quinone mono xime	2.5 to 9.0	470	-	Many cations and anions do not interfere	49
$\alpha$ -furyl- dioxime	pH 2.4	570	-	cu, Ni, Mn and Co interfere	50
2,2'-Dipyridyl ketoxime	4.5 to 5.8	335	$C = 1.9 \times 10^4$	-	51



1	2	3	4	5	6
Erichrome cyanine R	pH6	613	$\epsilon = 17300$	Pb, Hg(II), Sn(II), Cr(III) $I^-$ , $SCN^-$ , $NO_3^-$ interfere.	52
1-Phenyl-3-quinolyl-2-thiourea	4.2 to 9.8	425	-	Cu, Bi, Sb, Ag, EDTA, borate and oxalate interfere	53
Syn-phenyl-2-pyridyl ketoxime	Acetoxibic acid	475 and 550	-	Co and Ni strongly interfere	54
8-Hydroxy-7-nitroso quinoline sulphonic acid.	4.5 to 5-6.0	705	$\epsilon = 1.8 \times 10^4$ sensitivity is $0.003 \text{ cm}^{-2}$	Co(II) masked with citrate, tartrate, nitrate and thio-sulphate	55
2-formyl pyridine azine	4.0 5.0	660	$\epsilon = 0.29 \times 10^4$	-	56
2-(5-bromo-2-Pyridyl azo-5-diethylamino phenol	4.0	552	$\epsilon = 4.5 \times 10^4$	K, Mg, Na, Ca, Ni, $I^-$ , $F^-$ , $Cl^-$ , $S_2O_3^{-2}$ , $SO_4^{-2}$ interfere	57
2'-hydroxy-5'-methyl propiophenone oxime	8.5 to 9.5	500	-	$MoO_4^{-2}$ , $WO_4^{-2}$ , EDTA, Mn, Cr(III), Al	58

1	2	3	4	5	6
1(2-Quinolylazo) 2,4,5-trihydroxy benzene	8.0 to 10	510	$\epsilon = 1.86 \times 10^4$	Ce, Th, V(V), $\text{Cl}^-$ , $\text{I}^-$ , $\text{Br}^-$ , thiocyanate interfere	59
Biacetyl monoxime, 4-phenyl-3-thio- semicarbazone	4.0 to 9.3	350	-	-	60
2-Benzoyl pyridine 4-phenyl-3-thiosemi carbazone	pH 4.7	670	0.5 to 5 ppm	Pd, Cd, Ti(IV), Cu(II), Pd(II), V(V), Cr(III) interfere	61
2'-hydroxyl-5'- methyl acetophenone thiosemicarbazone	2.2	645	-	V(IV) and Cu(II) seriously interfere	62
Salicylaldehyde thiosemicarbazone	10	510	$\epsilon = 1.7 \times 10^3$	-	63
Di-2-Pyridyl ketone thiosemi- carbazone	pH 3.0	620	$\epsilon = 9.3 \times 10^3$	Complex is stable for at least 2 hrs.	64
2-Acetyl-pyridine 4-phenyl-3-thiosemi- semicarbazone	6.0	650	$\epsilon = 6.8 \times 10^3$	Cu(II), Ni(II), Co(II), Pd(II) EDTA, Cd(II) interfere	65

1	2	3	4	5	6
Bipyridyl glyoxal dithiosemicarbazone	2.5	550	2.0 to 9.0 ppm = $5.58 \times 10^3$	UO <sub>2</sub> (II) and V(V) strongly interfere	66
1(2-Pyridyl methy- lidene) amine1-5- (Salicylidene amine)	4.8	635	0 to 8 ppm	1:3 complex, Fe, determined in alloys and ores	67

## EXPERIMENTAL

### 1 Standard Iron Solution :

Standard iron solution 1 mg/ml was prepared from ferric chloride and the solution was standardized with EDTA volumetrically.<sup>76</sup> Further dilution for experimental purposes were made by diluting the stock solution with distilled water.

### 2 Reagent Solution :

0.055 gm 6-Me-QAT was dissolved in DMF and water (1:1) and diluted to 100 ml. The molarity of the solution is  $2.676 \times 10^{-4}$  M. The solution is found to be stable for more than a week.

### 3 Recommended Procedure :

To an aliquot of the solution containing upto 10 ppm of iron, and 1.5 ml of  $2.676 \times 10^{-4}$  M reagent solution, add 1 ml of 2 % ascorbic acid was added to solution to prevent atmospheric oxidation of iron and buffer solution of pH-5. Dilute this 10 ml with DMF and waters in volumetric flask. Measure the absorbance against reagent blank.

## RESULTS AND DISCUSSION

### Spectral Characteristics :

The absorption spectrum of the iron (III) 6-Me-QAT complex containing  $1.791 \times 10^{-3}$  M reagent at pH5 using reagent blank. Absorption measurements were made in the spectral region 350 to 600 nm and recorded in Table 4.2. From the graph, it was found that 380 nm will be suitable wavelength for the determination of iron. The molar absorptivity of the complex is  $8.319 \times 10^2 \text{ L Mole}^{-1} \text{ Cm}^{-1}$  at 380 nm.

Table 4.2

Molar Extinction Coefficients of Fe(III)

6-Me-QAT Complex

6-Me-QAT =  $2.676 \times 10^{-4}$  M and Fe(III) =  $1.791 \times 10^{-3}$  M

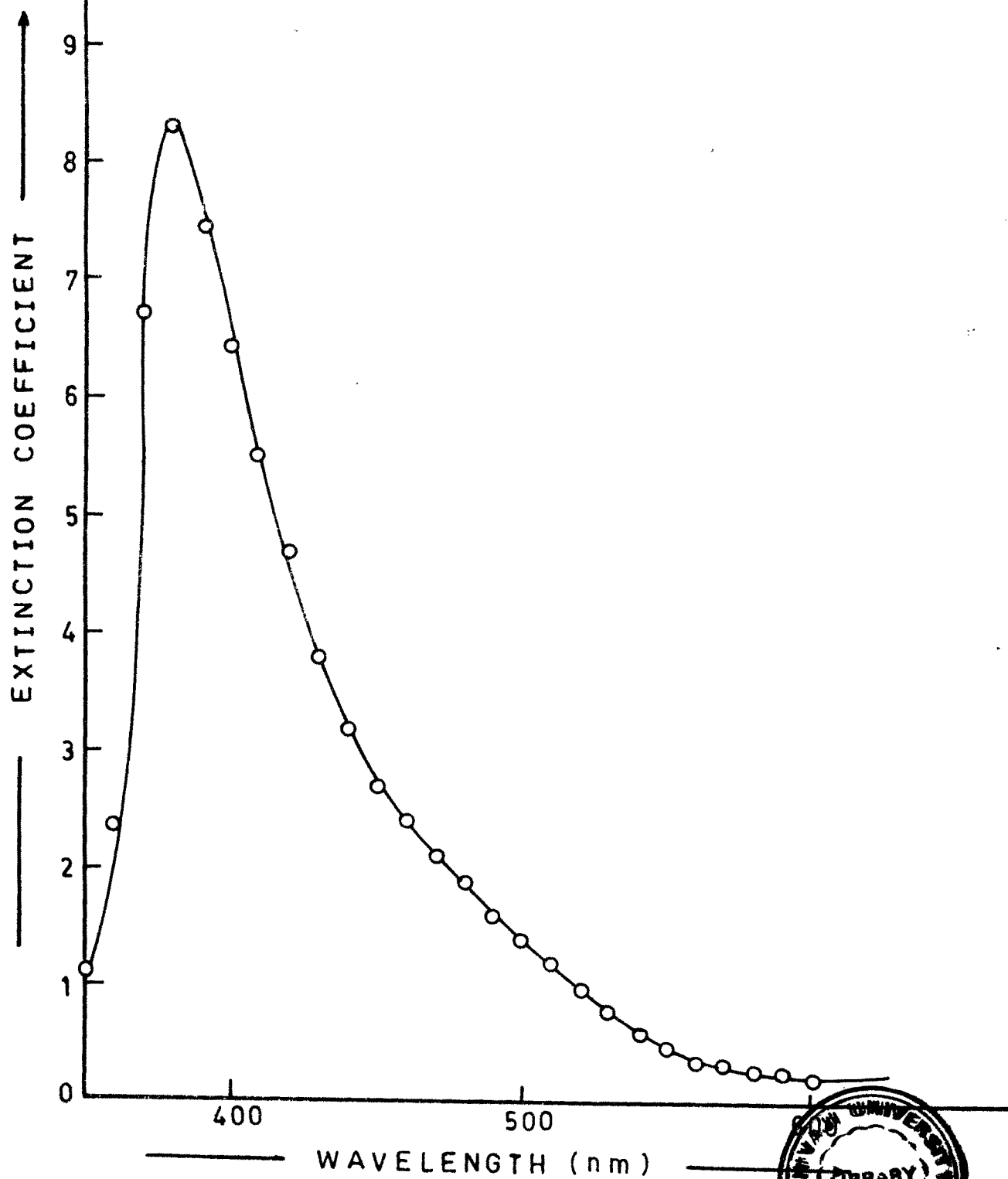
Wave length nm	Molar extinction coefficient of complex $\times 10^2 \text{ L Mole}^{-1} \text{ Cm}^{-1}$
350	1.172
360	2.428
370	6.722
380	8.319
390	7.409
400	6.476

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1	2
410	5.566
420	4.706
430	3.874
440	3.204
450	2.724
460	2.395
470	2.138
480	1.892
490	1.641
500	1.429
510	1.206
520	0.9826
530	0.943
540	0.6979
550	0.5862
560	0.4801
570	0.3964
580	0.3182
590	0.2568
600	0.2010

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FIG. 4-1 - ABSORPTION SPECTRUM OF  
Fe(III) - 6 Me - QAT COMPLEX .



Effect of Time on Absorbance :

In order to study the effect of time on the absorbance of iron (III) 6-Me-QAT complex containing  $1.791 \times 10^{-3}$  M Iron (III) at pH-5, the absorbance measurements were recorded at different time intervals at 380 nm. It was observed that there is instantaneous development of colour and the absorbance remains constant for 45 minutes and decreases after that.

Effect of Reagent Concentrations :

Solutions containing the same amount of Iron ( $1.791 \times 10^{-3}$  M) but different amounts of reagents varying from 0.2 ml to 0.9 ml of  $2.676 \times 10^{-4}$  M reagent solution were prepared. The pH5 buffer (1 ml) and 1 ml 2% ascorbic acid solution were added and the solution was made upto 10 ml with DMF water (1:1). Absorbance measurements were recorded at 380 nm against the simultaneously prepared reagent blank. The data given in table 4.3, Fig. 4.2 show that  $1.791 \times 10^{-3}$  M iron (III) solution required minimum 0.8 ml of  $2.676 \times 10^{-4}$  M reagent solution for maximum complexation. At higher concentration of the reagent there was insignificant increase in the absorbance. However, 0.9 ml of  $2.676 \times 10^{-4}$  M reagent solution was employed for the further studies to ensure maximum colour intensity of the iron complex.



Table 4.3

Effect of Reagent Concentration on the Absorbance of Fe-6Me-QAT complex.

$$\text{Fe} = 1.791 \times 10^{-3} \quad 6\text{-Me-QAT} = 2.676 \times 10^{-4} \text{ M}$$

Reagent ml	Absorbance of 380 nm
0.2	0.02
0.4	0.24
0.5	0.28
0.6	0.33
0.7	0.4
0.8	0.41
0.9	0.41

Effect of pH :

A series of solutions containing  $1.791 \times 10^{-3} \text{ M}$  Iron (III) and  $2.676 \times 10^{-4} \text{ M}$  of the reagent but varying in the pH from 1 to 10 were prepared and the absorption measurements were recorded at 380 nm. The results are summarised in Table 4.4. It was observed that maximum absorbance at obtained at pH 5. The absorbance of the solutions decreases at higher or lower pH values than this, which is shown in Fig. 4.3. Hence the pH 5 was maintained in the further studies.

Table 4.4

Effect of pH on the Absorbance of Iron(III)

6-Me-QAT Complex

(Fe) =  $1.791 \times 10^{-3}$  M    6-Me-QAT =  $2.676 \times 10^{-4}$  M

pH	Absorbance at 380 nm
1	0.06
2	0.4
3	0.18
4	0.379
5	0.490
6	1.250
7	0.475
8	0.02
10	0.26

Validity of Beer's Law and Sensitivity :

The solutions (final volume 10 ml) containing different amounts of iron (III) and the same amounts of reagents (final concentrations  $2.676 \times 10^{-4}$  M) with the pH maintained at 5 were used for the study. The absorption measurements were recorded against the reagent blank at 380 nm (Table 4.5, Fig. 4.4). Beer's law is obeyed upto a concentration of 5 ppm of iron (III). The Sandell sensitivity<sup>77</sup> of the reaction is  $0.016 \text{ ug/cm}^2$  of Fe(III). The Ringbom's plot ( Fig. 3.5) is indicated optimum range is 3 to 8 ppm of Fe(III).

Table 4.5

Variation of VALidity of Beer's law

6-Me-QAT =  $2.676 \times 10^{-4}$  M , pH = 5

Iron taken in ppm	Absorbance at 380 nm
0.1	0.06
0.2	0.125
0.3	0.24
0.4	0.46
0.5	0.63
0.6	0.71
0.7	0.8

FIG. 4.2 - EFFECT OF  
REAGENT CONC. ON  
Fe(III)-6 Me QAT COMPLEX.

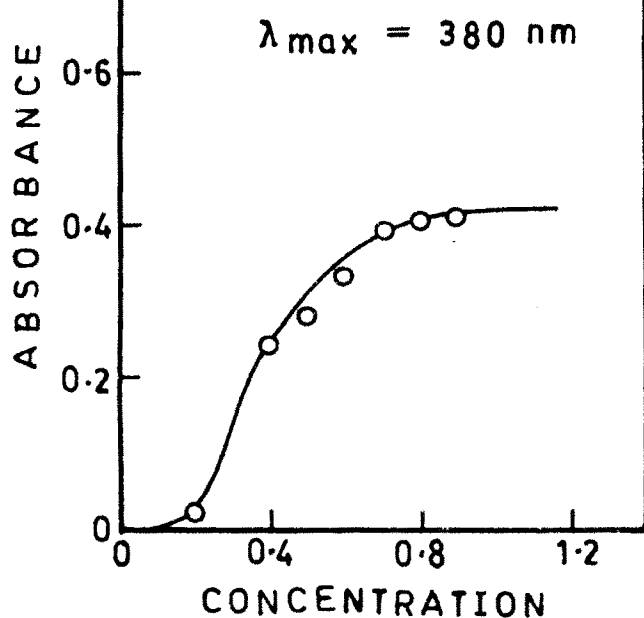


FIG. 4.3 - EFFECT OF PH  
ON Fe(III)-6 Me QAT  
COMPLEX.

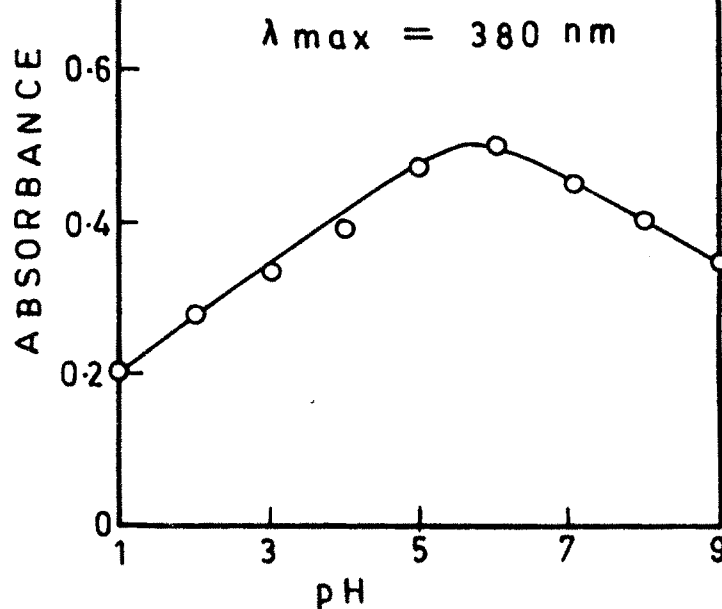


FIG. 4.4 - VALIDITY  
OF BEER'S LAW.

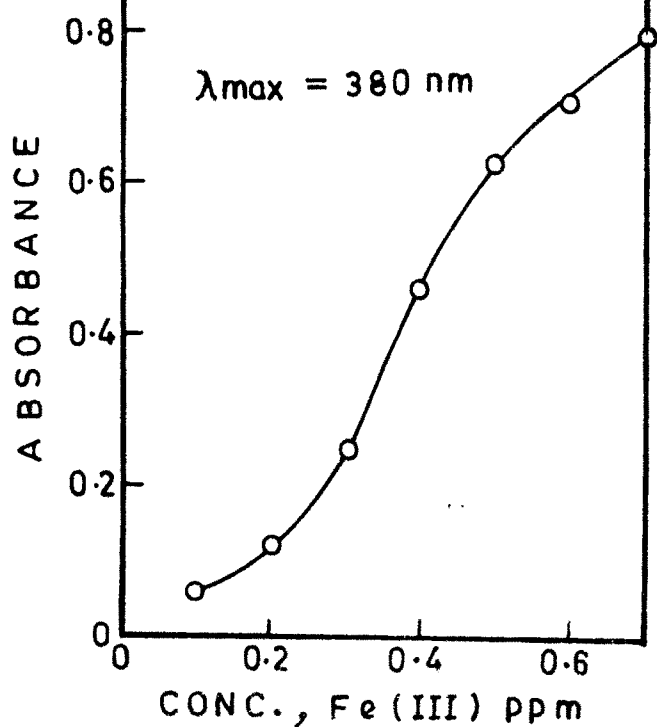
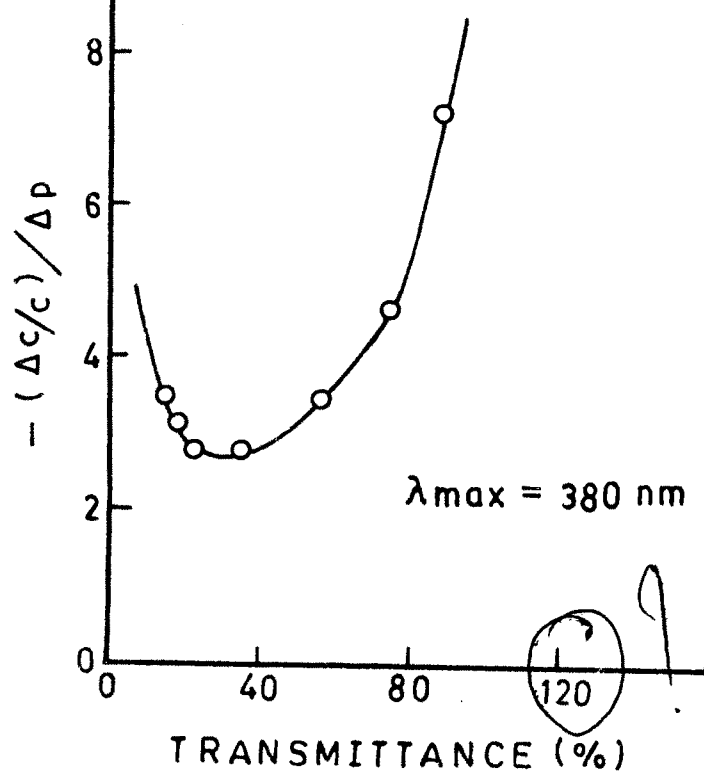


FIG. 4.5 -  
RINGBOM'S PLOT.



Composition of the Complex :

The combining ratio of metal to ligand (reagent) was ascertained by Job's method of continuous variations<sup>78</sup> and mole ratio method<sup>79</sup> for Job's method of continuous variation, a series of solutions were prepared by mixing equimolar. Solutions of iron (III) and the reagent (  $2.676 \times 10^{-4}$  M) The pH of the solution was adjusted to 5 the absorbances of the solutions after diluting to 10 ml in volumetric flask were recorded at 380 nm against simultaneously prepared reagent blank ( Fig. 4.5, Table 4.6). The plot indicates the existence of 1:1 complex with respect to metal and reagent represented as ML.

Table 4.6

Determination of the formula by Job's Method of Continuous Variation

$$(\text{Fe}) = (6\text{-Me-QAT}) = 2.676 \times 10^{-3} \text{ M, pH}=5$$

Metal ion ml	Reagent ml	Mole fraction of metal	Absorbance 380 nm
0.1	0.9	0.1	0.330
0.2	0.8	0.2	0.410
0.3	0.7	0.3	0.460
0.4	0.6	0.4	0.435
0.5	0.5	0.5	0.385
0.6	0.4	0.6	0.320
0.7	0.3	0.7	0.260
0.8	0.2	0.8	0.210
0.9	0.1	0.9	0.170

The dissociation constant of the complex  $k$  is calculated from the mole ratio plot by using the following equation :

$$K = \frac{\alpha C (n\alpha C)}{C (1 - \alpha)}$$

Where  $n = 1$

$C$  = Molarity of the solution of complex and

$\alpha$  = degree of dissociation defined by

$$\alpha = \frac{A_m - A_s}{A_m}$$

$A_m$  is maximum absorption obtained from horizontal portion of the curve and  $A_s$  is the absorbance of stoichiometric molar ratio of reagent to iron in the complex. The value of  $K$  comes out to be  $6.092 \times 10^{-11}$ .

#### Mole Ratio Method :

For mole ratio method, solutions containing the same final metal concentration ( $2.676 \times 10^{-4}$  M) and different amounts of the reagent ranging from  $5.380 \times 10^{-6}$  to  $3.766 \times 10^{-5}$  M concentration were prepared keeping the pH-5. Absorbance of the solutions were measured at 380 nm against the reagent blank. The curve showed break of the metal to reagent ratio 1:1 confirming the results obtained by the applications of Job's methods continuous variation ( Fig. 4.6 table 4.6), absorbance.

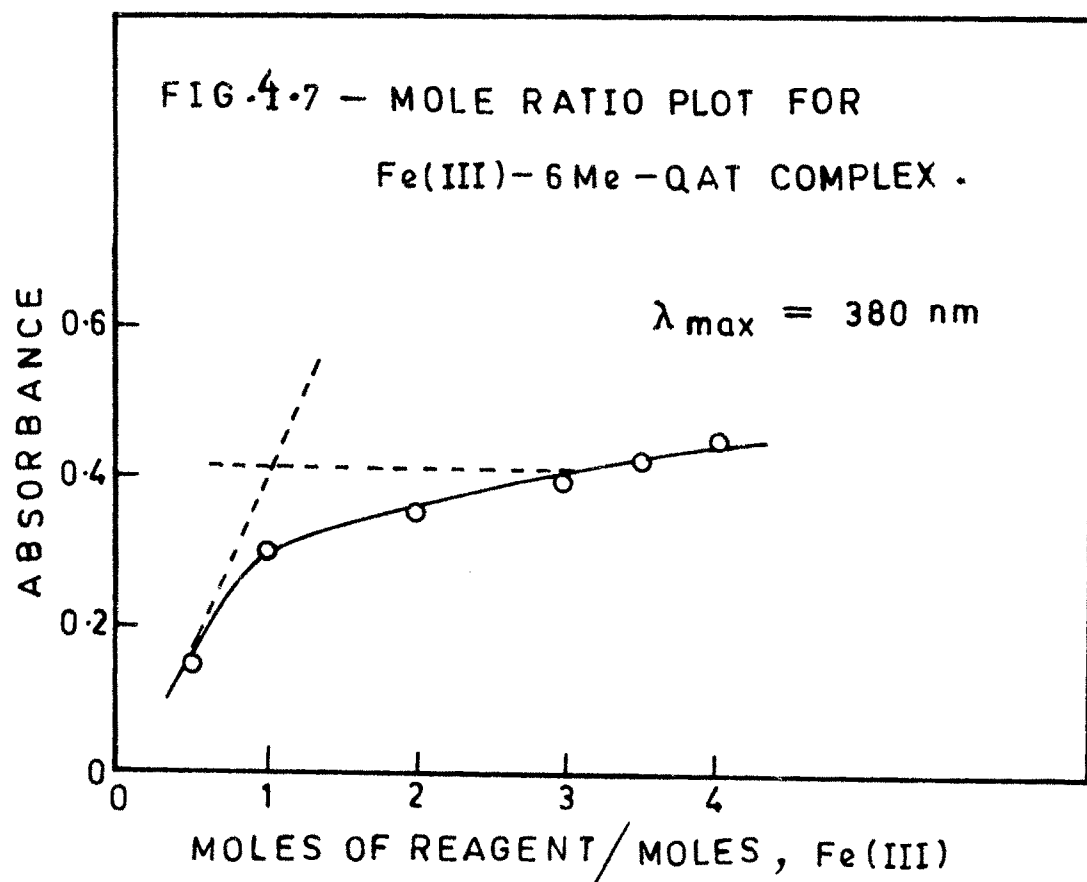
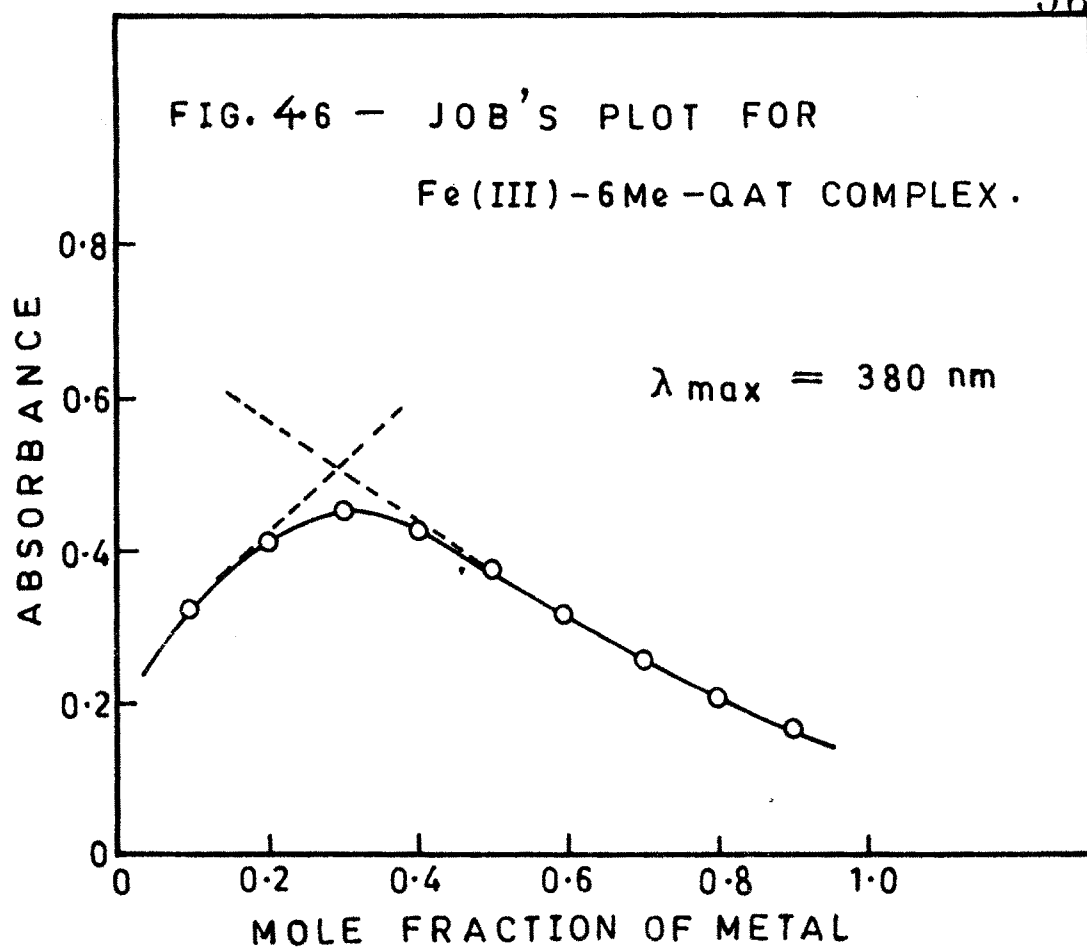


Table 4.7

Determination of the formula of Iron 6-Me-QAT complex by mole ratio method.

$$\text{Me-QAT} = \text{Fe} = 2.07 \times 10^{-4} \text{ M}$$

Metal ion ml	Reagent ml	Reagent metal ratio	Absorbance at 300 nm
0.2	0.2	0.5	0.15
0.2	0.4	1.0	0.30
0.2	0.8	2.0	0.35
0.2	1.2	3.0	0.4
0.2	1.4	3.5	0.42
0.2	1.6	4.0	0.45

Effect of diverse ion :

A number of representative ions were examined for their interference in the determination of iron as per the recommended procedure. The tolerance limit was assumed to be caused less than 2% error. Iron estimation is interfered seriously by where as Nickel, Cerium and Copper tolerate at tracer concentration. The tolerance for the various foreign ions tested has been shown in Table 4.8.



Table 4.8 : Effect of diverse ions

$$\text{Fe(III)} = 1.791 \times 10^{-3} \text{ M}$$

$$6\text{-Me-QAT} = 1.02 \times 10^{-3} \text{ M}$$

Metal ion	Tolerance limit, PPM
Zn(II)	15
Co(II)	10
Ni(II)	5
Mn(II)	15
Ba(II)	30
Ce(IV)	5
Cu(II)	5
Mg(II)	10
Cd(II)	20
Sn(II)	none
Cr(W)	10
V(V)	200
Acetate	30
Fluoride	50
Chloride	250
Citrate	25

# REFERENCES

- 1      Goswami, S.D. Patel, B.M. and Patel, Bipin ( Dept.  
Chem. P.J. Sci. Coll Bardolin, Surat, India), J. Inst.  
Chem. (India) 54, 111-112, (1982).
- 2      Chen. Yongzhao, and Chen, Huanguang Goa Teng Hsueh  
Hua Hsueh Hsueh, Rao 3, 319-326 (1982).
- 3      Satake, Mastada, Mehra, Mool C, and Fujinga, Taitiro,  
Bull.Chem. Soc. Jpn. 55, 2079-2082 (1982).
- 4      Zhang, Rongcan and Zhu, Xiaohua, Fen Hsi Hua Hsueh,  
9, 499 (in Chinese) (1981)
- 5      Glushkova, I.N. and Ketova, L.A. Org. Reagenty Anal.  
Khim, 3 6-11 (in Russian). (1960)
- 6      Nomura, Tsuyoshi, J. Electroanal. Chem. Interfical  
Electrochemistry, 124, 213-219 (1981).
- 7      Harvey, David T. and Linton, Richard W. Anal. Chem  
53, 1684-1688 (1981)
- 8      Panasenko, T.D., Vistyak, L.T. and Sakharova T.V.,  
Khim, Promst, Ser. Methody Anal. Kontrolya Kach, Prod,  
Sti, 3, 35-37 (In Russian), (1981).
- 9      Chermukhim E.P., Solenok, N. . and Vistyak L.T., Khim  
Prom-St, Ser. Metody Anal, Kontrolya Kach. Prod.Khim,  
Prom-Sti, 3, 23-25 (In Russian), (1981)

- 10 Yones, M. and Gruzleski, I.E. Trans. Am, Foundrymen's Soc. 88 737-744, (1980)
- 11 Liu. Hsao-Pu, Fen-Hsi Hua Hsueh 8, 258-260 (in Chinese) (1980).
- 12 Farag, Abdel-Fattah Bastawi, El-Wakil Ahmed Mohamad, and El. Shahawi, Mohamad Sorour, Ann. Chim, (Rome) 72, 103-106 (1982).
- 13 Pal, A.K. Datta, A, Ghosh, J.B. and Amalraj, M., J. Inst. Chem. (India) 54 5-6, (1982).
- 14 Leggett, d.J., Chen, N.H. and Mahadevappa D.S. Indian J.Chem., Sect. A, 20, 1051-1953, (1981)
- 15 Maljkovic, Darko; Maljkovic, Dubravka and Hedzet, J. Microchem, J. 27 6-12, (1982)
- 16 Moseev, N. and Gritsenko, E. Poligratiya, 10, 16-18 (in Russian), (1981)
- 17 Nikitina, O.I., Antipenko, L.L., Ivanova, N.K. Butko, N.I. and Fedorova E.V., Zavod, Lab. 48, 36-37, (1982)
- 18 Pande, K.K. and Likhar J.V., J.Indian Chem. Soc. 57, 109-110 (1980)
- 19 Thompson, K.C.; and Wagstatt K, Analyst (London) 105 641-650, (1980)
- 20 Boniface, H.J. and Jenkins R.H. Analyst (London), 105 705-712, (1980)

- 21 Nikolaeva, L.N., Komissarova, T.E. and Pakhomova, T.M.  
Zh. Anal. Khim, 35, 1148-1151 (1980)
- 22 Singh, Devender and Singh, H.B.J. Inst. Chem. (India)  
52 243-249, (1980)
- 23 Taketatsu, Tomitsugu and Sato, Atsuko Bull. Chem-Soc.  
Jpn. 53, 3713-3714, (1980)
- 24 Garcia de Torres, A, Reina E. Cano Pavon, J.M.  
Valcacel, and M. Afinidad 37 51-52 (1980)
- 25 Kawashima, Takuji, Hatakeyama, Naoko, Kamada,  
Masaakira and Nakono, Shigenori, Nippon Kagaku Kalishi  
1, 84-90, (1981)
- 26 Pandell A.J.; Mantgomery, R.A., and Meissner R.A.,  
Analyst (London) 105, 181-183, (1980)
- 27 Dieker, J.W. and Vander Linden, W.E., Anal. Chem.  
Acta, 114, 267-274 (1980)
- 28 Graciani, C.E., An. Quim. 67, 607, (1971)
- 29 Notenboom H.R., Holland W.J. and Soules, J. Mitrochim.  
Acta., 1, 187, (1973)
- 30 S.Takyoshi and S. Ikuko, J. Chem. Soc. Japan Pure  
Chemistry Section, 87, 372 (1966)
- 31 Gracioni C.E., Cardenas J. and Nieto F. An Quim.,  
70, 695, (1974).

- 32 Vassiliades C. and Manoussakis G., Bull Soc. Chem. France, 2 , 390 (1960)
- 33 Wakimoto S., Japan Analyst., 10, 968 (1961)
- 34 Marczenko Z. and Kasiura, K., Chem. Anal. Warsaw, 6, 37 (1961)
- 35 Alduan a., Castilla J.L., Suarez J.R. and Cacho Palomer, J.F. Rev. Acad. Cienc. Exacts, Fis Quim Nat. Zaragoza, 31, 91 (1976)
- 36 Smith A.N., Analyst, 84, 516 (1959)
- 37 Ayres G.H. and Roach H.K., Anal. Chim. Acta., 26, 332 (1962)
- 38 Khopkar, S.M. and De, A.K., Anal. Chim. Acta., 22, 223 (1960)
- 39 Hassan E.K. and Saad, E., Z. Anal. Chem., 34 1382, (1962)
- 40 Mikhelson P.B., Bozyak A.K. and Mashkovshkaya L.T., J. Analyt. Chem. USSR, 26, 686 (1971)
- 41 Poddar S.N., Ind. J.Chem., 1, 496 (1963)
- 42 Prakash, O. and Mursharn S.P., Chem, Analyst., 49, 473 (1967)
- 43 Van Urk H.W., Pharm. Weekblad, 63, 1121 (1926)
- 44 Howe D.E., and Mellon M.G., Ind. Engg., Chem., Anal. Ed., 12, 448 (1940)

- 45 Backwith R.S., Chem. Ind., 663 (1954)
- 46 Korrnaga, Motomizu and Toei, Anal. Chem. Chim, Acta, 65, 335 (1973)
- 47 Gallego M., Garcia Vargas M., Volcarcel M., Analyst, 104, 613 (1979)
- 48 Stephens B.G., Fulkel H.L., Jun and Spinell W.M., Anlyst, Chem., 46, 692 (1974)
- 49 Mulye R.R. and Khopkar S.M., Z. Analyst, Chem., 272, 283 (1974)
- 50 Valcorcel M., Martinez M.P. and Pino F., Analyst, 100, 33(1975)
- 51 Garcia de Torres, A. Canno Pavan, J.M. Castaneda F. Mikrochim, Acta, 3 (5-6), 375 (1984)
- 52 Patroescu and Cojocar, Revta Chim. 27, 444(1976)
- 53 Makoto Otomo, Anal. Chim. Acta, 116, 161 (1980)
- 54 Kamil F.,Sindhvani S.K. and Singh R.P., Ind. J.Chem. Sect. A., 16, 365(1978)
- 55 Patil P.S. and Shinde V.M., Mikrochim. Acta, 7, 151(1977)
- 56 Ceba M.R., Nevadic J.B. and Mansilla A.E., Talanta, 28, 134(1981)
- 57 Yashiu S., Bull Chem. Soc. Japan, 48, 2793(1975)
- 58 Mathur S.P. Ann. Quim, 74, 1020(1978)

- 59 Kawatkar S.G. and Bhaskare S.K. Talanta, 22, 189,(1975)
- 60 Ceriatti G. and Spandriol., Anal. Chem. 33, 579(1961)
- 61 Shivahare G.C., Mathur S. and Mathur M.K., Z.Anal.Chem., 261, 126(1972)
- 62 Abbasi S.A., Bhat B.G. and Singh R.S., Ind. J.Chem. A, 14, 215(1976)
- 63 Lague de Castro M.D. and Valcarcel M., Analyst, Lett., 11,11(1978)
- 64 Aliz Abu-Zuhri, Ind. J. Chem., 222, 909(1983)
- 65 Prakash Dutt and Singh R.P., Mikrochim. J., 18, 412(1973)
- 66 Ishwar Singh, Mrs. Poonam and P.S. Kadya, Talenta, 32, 387(1985)
- 67 J.M.Cano Pavon, J.C. Jimenez Sancher and F. Pino, Anal. Chem. Acta, 75, 335(1975)
- 68 M.T. Martinez Aguilar and S.M. Cano Pavon, Mikrochimic Acta, 1, 631(1977)
- 69 M.C. Patel, J.R.Shah and R.P.Patel, J.Ind. Chem.Soc. 50, 560(1973)
- 70 D. Perez, Bendito and F.Pino Perez, Mikrochimica Acta, 1, 613(1976)
- 71 M.P. Martinez, M. Valcarcel and F. Pino, Anal. Chim. Acta, 81, 157 (1976)

- 72 M.T.Marinez Aguilar J.M. Cano Paron and F. Pino, Anal. Chim. Acta., 90, 335(1977)
- 73 Khasanis D.V. and Shinde V.M. Chemica Analit. (Warsaw) Communicated.
- 74 J. Lopez Bahamonde, D.P. Bendito and F. Pino., Talenta, 20, 694(1973)
- 75 Rosales, Daniel, Gamez, Ariza, Jose L., Munoz Leyva, Juan A., Mikrochim, Acta, 1(1-2) 77 (1985)