**CHAPTER IV**

**SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE, IRON, COBALT AND NICKEL**

**A. MANGANESE**

The oxidation states for manganese in which it occurs in compounds are +II, III, IV, VI and VII. The +VII state occurs only in the oxo compounds \( \text{MnO}_4^- \), \( \text{Mn}_2\text{O}_7 \) and \( \text{MnO}_3^- \). The hydroxide \( \text{Mn(OH)}_2 \) precipitates at pH \( \approx 8.5 \) and exhibits no amphoteric properties. On standing in air, the white \( \text{Mn(OH)}_2 \) precipitate slowly darkens as it is oxidized to hydrous manganese dioxide. Manganese (II) forms complexes of low stability with EDTA, cyanide, tartrate and ammonia.

**Spectrophotometric reagents for manganese:**

The well known and often-used spectrophotometric method for the determination of manganese which is based on the coloured permanganate ion is highly selective but rather insensitive (1-3). One of the important class of reagents among the various spectrophotometric reagents known for manganese is the compounds derived from quinoline which includes 8-aminoquinoline (4), 8-hydroxyquinoline (5,6), 5,7-dichloro-8-hydroxyquinoline (7), 8-mercaptoquinoline (8) and 8-hydroxyquinoline-5-sulphonic acid (9). Some thiocarbamates have been reported as spectrophotometric reagents for manganese in which diethylidithiocarbamate (10,11),
morpholinium-3-oxapentaethylendithiocarbamate (12), piperidinium pertamethylidithiocarbamate (13) are important. Some important oximes used as reagents for the purpose are formaldoxime (14, 15), acetaldoxime (16), 2,6-pyridinedialdoxime (17), salicylaldoxime (18) and 5-chloro-2,4-dihydroxypropiophenone oxime (19). Among hydrazones are salicylaldehyde isonicotinoyl hydrazone (20) and salicylaldehyde benzoyl hydrazone (20).

Some other important reagents proposed for the purpose are diethylaniline (21), NN**N*-tetrakis (2-hydroxypropyl)ethylene diamine (22), \( \alpha, \beta, \gamma, \delta \)-tetrakis(4-carboxyphenyl)porphine (23), benzohydroxamic acid (24), anthranilohydroxamic acid (25), 6-methoxy-2-methylthiopyrimidine-4-carboxylic acid (26), nicotinohydroxamic acid and isonicotinohydroxamic acid (27), pyridine 2,6-dicarboxylic acid (28), 2-thienyltrifluoroacetone (29), dithizonepyridine (30), 1,10-phenanthroline (31), pyridine thiocyanate (32), thiothienyltrifluoroacetone (33), methyliminodimethylene phosphonic acid (34), 1,10-phenanthroline in the presence of tetraiodofluorescein (35), isophtaldihydroxamic acid (36), diantipyril methane (37), and potassium trithiocarbonate (38).

Some important basic dyes which can be named are leucomalachite green (39), malachite green (40), calcichrome (41), rhodamine 6G (42), indigo carmine (43), xylenol orange (44) and zincon (45).
A few heterocyclic azo dyes are known as spectrophotometric reagents for the determination of manganese. Two important azo dyes are 1-(2-pyridylazo)-2-naphthol (46) and 4-(2-pyridylazo)resorcinol (47). Some other azo dyes used for the purpose are 4-(2-thiazolylazo)-resorcinol (48), 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (49), N,N-dimethyl-p-(2-pyridylazo)aniline (50), 2-(2-pyridylazo)-p-cresol (PAC)(51) and 1-(2-quinolylazo)-2,4,5-trihydroxybenzene (52).

**Present work:**

Preliminary investigations showed that the addition of aqueous solution of THT to manganese (II) ions results a dark brown coloured complex instantaneously at neutral pH. This colour reaction has been investigated in detail with a view to ascertain its potentiality for spectrophotometric determination of manganese (II).

**Experimental**

**Manganese (II) solution:**

A stock solution of manganese (II) was prepared by dissolving an appropriate amount of manganese chloride dihydrate (AnalaR) in acidulated double distilled water. The solution was standardized complexometrically with EDTA using eriochrome black T as indicator (53).
A phosphate buffer (pH 6.2) (53) was prepared by diluting 250 ml of 0.2M potassium dihydrogen phosphate and 43 ml of 0.2M sodium hydroxide to 1 l with distilled water.

All chemicals used were of analytical-reagent grade.

Spectral behaviour of the complex and effect of pH:

A series of solutions containing 1.0 ml of $2 \times 10^{-4}$M manganese (II) and 1.0 ml of $1 \times 10^{-3}$M THT were prepared and pH's were adjusted at different levels in a total volume of 25 ml in distilled water. Absorption spectra of the solutions were recorded against corresponding reagent blanks. It has been observed that only one complex is formed at all pH values, absorbing maximum at 520 nm (fig. IV.1).

Plot of pH vs. absorbance at the $\lambda_{\text{max}}$ 520 nm of the complex shows that constant and maximum absorbance is exhibited in the pH range 5.8 - 7.3 (fig. IV.2). Subsequent studies have been carried out in a phosphate buffer (pH 6.2) and 2.0 ml of the buffer was used to maintain this pH value. The colour of the manganese (II) - THT complex formed remains stable for 24 h at room temperature.
FIG. IV.1. ABSORPTION SPECTRA OF Mn(II) - THT COMPLEX AT DIFFERENT pH

FIG. IV.2. EFFECT OF pH ON Mn(II) - THT COMPLEX
**Effect of reagent concentration:**

The effect of reagent concentration on complex formation was studied by preparing a series of solutions containing a fixed amount of manganese (II) (1.0 ml of 2x10^{-3}M), varying amounts of reagent and 2.0 ml of phosphate buffer (pH 6.2) in a total volume of 25 ml. The absorbance was measured at 520 nm. It was observed that at least two times molar excess of THT was required for complete complexation (fig. IV.3). In subsequent studies, five times molar excess of the reagent was used.

**Physico-chemical characteristics of the complex:**

Linearity between the absorbance of the complex and manganese (II) concentration was examined by varying the concentration of manganese (II) in the solutions containing a fixed amount of ligand (sufficient excess) at pH 6.2 and measuring the absorbance at 520 nm against the corresponding reagent blank. The results obtained for the validity of Beer's law, optimum range of concentration for accurate determination as calculated from Ringbom plot (fig. IV.4), sensitivity and molar extinction coefficient of the complexation reaction are summarised in table IV.1.

**Table IV.1: Physico-chemical constants of the manganese(II)-THT complex.**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \lambda_{\text{max}} )</td>
</tr>
<tr>
<td>2.</td>
<td>Beer's law range</td>
</tr>
</tbody>
</table>
ABSORBANCE

MOLES OF REAGENT

FIG. IV. 3. EFFECT OF REAGENT CONCENTRATION ON Mn(II) - THT COMPLEX

Log ppm

FIG. IV. 4. RINGBOM PLOT FOR Mn(II) - THT COMPLEX

Mn(II) = 8 \times 10^{-6} \text{ M}
3. Optimum concentration range 0.16-1.0 ppm
4. Sandell's sensitivity 0.001 (μg Mn(II)/cm²)
5. Molar extinction coefficient (€) 5.5x10⁴ (l.mol⁻¹ cm⁻¹)
6. Molar composition by Job's method (fig. IV.5) 2:3 (Mn:Li)

Recommended procedure:

To an aliquot containing 4-25 μg of manganese (II) ion, add excess of THF solution (at least 5 molar times) followed by 2 ml of phosphate buffer of pH 6.2 to adjust pH. Dilute to 25 ml with double distilled water. Measure the absorbance at λmax 520 nm against a reagent blank prepared in a similar way. The amount of manganese present can be evaluated from the calibration curve drawn under similar conditions.

Absorbance deviations and accuracy of the method:

The mean absorbance of a series of ten solutions containing 2x10⁻⁶M of manganese (II) and excess of THF in total volume of 25 ml at pH 6.2 was found to be 0.44, with a standard deviation of 0.0027.

The accuracy of the method was checked by preparing a series of ten solutions of different amounts of manganese(II) in the range 4-25 μg and a fixed and excess amount of THF at pH 6.2 in a total volume of 25 ml. The percentage error of the results of this series obtained was in the range 0.19-1.7%, which showed the fair accuracy of the method.
FIG. IV.5. COMPOSITION OF Mn(II) - THT COMPLEX BY JOB'S METHOD

TOTAL MOLARITY

= $6 \times 10^{-5}$ M
**Effect of diverse ions:**

In the determination of manganese at the 0.55 μg/ml level, chloride, fluoride, iodide, nitrate, nitrite, thiosulphate, sulphide, sulphate, cyanide, thiocyanate, citrate, tartrate, borate, oxalate, thiourea, thiosemicarbazide, phosphate, alkaline earths, lanthanides, aluminium (III), chromium (III), vanadium (V), molybdenum (VI), tungsten(VI), and gold, platinum metals did not interfere at all. Results of tolerance limits, in parts per million of various ions in solution that caused a deviation smaller than ± 2% in absorbance, are described in table IV.2

**Table IV.2: Effect of diverse ions**

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Amount tolerated (ppm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA</td>
<td>240</td>
<td>-</td>
</tr>
<tr>
<td>Zinc (II)</td>
<td>33</td>
<td>masked by EDTA</td>
</tr>
<tr>
<td>Cadmium (II)</td>
<td>35</td>
<td>masked by EDTA</td>
</tr>
<tr>
<td>Mercury (II)</td>
<td>50</td>
<td>masked by CN⁻ or EDTA</td>
</tr>
<tr>
<td>Iron (II)</td>
<td>30</td>
<td>masked by CN⁻ or EDTA</td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>30</td>
<td>masked by CN⁻ or EDTA</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>25</td>
<td>masked by CN⁻ or EDTA</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>25</td>
<td>masked by S₂O₃⁻</td>
</tr>
<tr>
<td>Silver (I)</td>
<td>50</td>
<td>masked by CN⁻</td>
</tr>
<tr>
<td>Lead (II)</td>
<td>50</td>
<td>masked by S₂O₃⁻</td>
</tr>
</tbody>
</table>
Discussion:

Reagents for spectrophotometric determination of manganese (II) are very few in number in comparison to those for common transition metals.

Most widely used method for the determination of manganese are based on the oxidation of manganese (II) to manganese (VII)\(^{(1-3)}\) but because of low sensitivity these methods are not considered useful for trace analysis. With persulphate as oxidant, it is necessary to add a small amount of silver or cobalt ions to catalyse the oxidation. The oxidation with periodate is carried out in sulphuric acid or nitric acid, but the concentration of the acid affects the rate of oxidation. Reducing species, including chloride, present in the solution interfere seriously and they should be removed. Large amounts of coloured metal ions are also found to interfere.

8-Aminoquinoline\(^{(4)}\) when oxidised by permanganate, the highly coloured oxidation product is stable at an
appropriate wavelength. Beer's law is followed by 0.6-27.5 μg of manganese in 50 ml. There is interference by ferric, pentavalent vanadium, ceric and chromate ions.

With diethylidithiocarbamate (10, 11), colour development is carried out in ammonium citrate-ammonium hydroxide medium at pH 7.5-8.0 and manganese is extracted with chloroform or isobutyl acetate as the diethylidithiocarbamate complex but the extraction procedure is very complex in presence of various metal ions. For example, iron is first extracted with chloroform as the 1,10-phenanthroline-ferrous complex, then copper is extracted into butyl acetate with addition of sodium diethylidithiocarbamate. The aqueous phase is made alkaline, extracted with chloroform and extract is discarded. Addition of sodium diethylidithiocarbamate forms the manganese complex in aqueous phase, which is then extracted in isobutyl acetate.

When formaldoxime (14, 15) is used as reagent for manganese (II), iron and nickel interfere. In analysis of perchloric acid or trichloro acetic acid extracts of biological materials, the absorption of yellow ingredients reduces the accuracy of determination by formaldoxime. Cyanide also retards colour development.

Benzohydroxamic acid (24) is found to be more sensitive reagent for manganese, but the disadvantage in
that this case is both valence of iron and cobalt interfere and excess of cyanide, tartrate and EDTA prevent colour formation.

The yellow chelate of manganese with 2-thenoyl trifluoroacetone (29) is extractable with a mixture of acetone-benzene. The extraction is quantitative at pH 6.7-8.0. There is interference by 0.2 mg of chloride, by 1 mg of arsenic, molybdenum or vanadium and by 5 mg of copper or titanium. Cobaltous ion and EDTA also interfere seriously.

Potassium trithiocarbonate (38) is another recently used reagent for manganese (II). Serious interferences of Bi(III), Cu(II), Fe(III), and Ni(II) could be suppressed by the addition of sodium citrate and potassium cyanide.

Leucomalachite Green (39) is used indirectly in the determination of manganese. Manganese ions are oxidized to permanganic acid by periodate at room temperature. Then the leucomalachite green added is oxidized and colour intensity is read at 620 nm. However, it gives 200 fold sensitivity over the permanganate colour, but ferrous and ferric ions interfere seriously and must be removed. On the other hand, the reading is also increased by chromate, dichromate, iodide, oxalate and thiosulphate and decreased by reducing agents such as nitrite and sulphate.

In the presence of excess 1,10-phenanthroline, the manganese (II)-1,10-phenanthroline with tetraiodofluorescein
was quantitatively extracted into ethyl acetate from an ammonium buffer solution while the other metal -1,10-phenanthroline complexes were not quantitatively extracted under the same conditions (35). The extraction method was applied to spectrophotometric determination of manganese (II).

Among heterocyclicazo dyes, 1-(2-pyridylazo)-2-naphthol (46) is a sensitive spectrophotometric reagent. Manganese forms a wine-red chelate with it in alkaline solution. with 4-(2-pyridylazo)resorcinol (47), manganous ions form a 1:3 complex at pH 9.7-10.7. However, Fe(II), Co(II), and Ni(II) interfere seriously. Moreover, in both cases when these interfering metals are present the manganese is determined by difference, by destruction of the manganese complex.

In the present method for the determination of manganese (II) spectrophotometrically, complexing agents such as DTA and cyanide do not interfere and these have been used to mask most of the interfering transition metals viz. zinc(II), cadmium (II), mercury(II), iron(II), cobalt (II), nickel(II) and silver(I). Indium(III), antimony(III) and bismuth(III) have been masked with sulphide while thorium with phosphate. Thiosulphate was used to mask lead (II) and copper(II). On the other hand, the method is very simple and highly sensitive which can be judged by comparing the sensitivity of the method with some well known methods (Table IV.3).
<table>
<thead>
<tr>
<th>Reagent</th>
<th>Molar extinction coefficient (ε)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.8x10^3/550 nm</td>
<td>4.</td>
</tr>
<tr>
<td>8-Aminoquinoline</td>
<td>1.1x10^3/580 nm</td>
<td>5.</td>
</tr>
<tr>
<td>Formaldoxime</td>
<td>1.12x10^4/455 nm</td>
<td>14, 15</td>
</tr>
<tr>
<td>1-(2-Pyridylazo)-2-naphthol (PAN)/CHCl₃/ C₆H₆</td>
<td>4.8x10^4/562 nm</td>
<td>46.</td>
</tr>
<tr>
<td></td>
<td>4.7x10^4/568 nm</td>
<td></td>
</tr>
<tr>
<td>4-(2-Pyridylazo)-resorcinol PAR/CHCl₃</td>
<td>4x10^4/550 nm</td>
<td>47.</td>
</tr>
<tr>
<td>N,N-Dimethyl-p-(2-pyridylazo)-aniline</td>
<td>3.27x10^4/540 nm</td>
<td>50.</td>
</tr>
<tr>
<td>2-(2-Pyridylazo)-p-cresol (PAC)/CHCl₃</td>
<td>1.8x10^4/560 nm</td>
<td>51.</td>
</tr>
<tr>
<td>1-(2-Quinolylazo)-2,4,5-trihydroxybenzene</td>
<td>4.6x10^4/560 nm</td>
<td>52.</td>
</tr>
<tr>
<td>Tris[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt</td>
<td>5.5x10^4/520 nm</td>
<td>Present method</td>
</tr>
</tbody>
</table>

Table IV.3: Comparison of sensitivities of various spectrophotometric reagents for manganese (II)
B. IRON

Iron with electronic configuration $3d^6\ 4s^2$, shows most frequently +2 and +3 oxidation states. Iron is generally octahedral in its compounds though some tetra-co-ordinate compounds also exist. The tendency to form complexes is generally greater with Fe(III) than with Fe(II). Ligands (pyridine, phenanthroline etc.) having sufficiently strong ligand fields, bring about electron pairing in 3d orbitals forming stable low spin Fe(II) complexes, while oxygen containing ligands (which have comparatively weak ligand fields) form stable high spin Fe(III) complexes. This may be attributed to the favourable energy associated with the symmetrical singly occupied d orbitals in the high spin $d^5$ configuration.

Spectrophotometric reagents for iron:

Reagents, known for spectrophotometric determination of iron, have been reviewed by several workers (1-3, 54-57). A critical review of reagents containing iron (II) specific group

![Chemical structure](image)

has been given by Schilt (57). Some important reagents which can be included for the spectrophotometric determination of
Iron are the classical thiocyanate method coupled with extraction (1-3), 1,10-phenanthroline and 2,2'-bipyridyl (1-3), bathophenanthroline (58), 4,7-dihydroxy-1,10-phenanthroline (59), sulphosalicylic acid (2), 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine (60), 2,6-bis(4-phenyl-2-pyridyl)-4-phenyl pyridine (61), 2,2'-dipyridyl ketone-2-pyrimidyl hydrazone (62), 2,4-diamino-5-nitrosopyridazinol (63), 3-[(4-sulphophenyl)-2-pyridyl]5-(4-sulphophenyl)-1,2,4-triazine (64), 2-pyridylaldehyde-2-pyridyl hydrazone (65), di-2-pyridylglyoxal-2-quinolyl hydrazone (66), 3-(1-isoquinolyl)-5,6-diphenyl-1,2,4-triazine and 3,3'-bis(5,6-diphenyl-1,2,4-triazine) and their sulphonated derivatives (67), 2,2'-dipyridylmethanone-2-pyrimidylhydrazone (68), 4,5,7-trihydroxy-3-(p-methoxyphenyl)coumarin (69), 1,3-bis-[(2-pyridyl)methyleneamino]-thiourea and 1,3-bis-(2-pyridylmethyleneamino)guanidine (70), sodium rhodizonate (71), thioglycolic acid (72), 2,2'-dipyridyl ketoneaminomethylimine (73), 2-[(di-(2-pyridyl)-methylidine hydrazone]pyrimidine (74) and pyridine-2-aldehyde guanyl hydrazone (75), violuric acid (76), tiron and aniline (77), ferrozine (78) and acetylacetone (79).

Triphenylmethane dyes are sensitive reagents for the spectrophotometric determination of iron. Some of these or of this type of dyes are xylenol orange (80), pyrocatechol violet (81), chromazurol S and eriochrome cyanine R with some cationic surfactants (82), methylene blue (83), aniline blue (84) and bromopyrogallol red + hexadecyltrimethyl ammonium bromide (85).
Several oximes and thiosemicarbazones recommended for determination of iron have been reviewed by Singh et al. (55,56). Some sensitive oximes listed therein are: 2,2'-dipyridyl ketoxime (86), 2,6-diacetyl pyridine dioxime (87), diacetyl monoxime (88), 3-hydroxy-2-methyl-1,4-naphthoquinone monoxime (89) and diimine dioximes (90). Among thiosemicarbazones, important reagents are picolin-aldehyde thiosemicarbazones (91), 2-acetylpyridine-4-phenyl-3-thiosemicarbazone (92), bipyridyl glyoxal dithiosemicarbazone and 2-(3-sulpho-benzoyl)pyridine thiosemicarbazone (93), phenanthrenequinone monothiosemicarbazone (94) and quinoline-2-aldehyde thiosemicarbazone (95).

Heterocyclic azo dyes are an important class of reagents for the determination of iron. 1-(2-pyridylazo)-2-naphthol (96,97) and 4-(2-pyridylazo)-resorcinol (98,99), are important among these. Some other heterocyclic azo dyes used for the purpose are 4-(2-thiazolylazo)-resorcinol (100), 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (101), 2-(pyridylazo)chromotropic acid (102), 1-(5'-chloro-2',3'-dihydroxypyridyl-4'-azo)benzene-4-sulphonic acid (103), 2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)aniline (104), 2-(2'-thiazolylazo)-5-diethylaminophenol (105), 5-(3,5-dibromo-2-pyridylazo)-2,6-diaminotoluene (106), 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (107), 4-(4-methyl-2-thiazolylazo)resorcinol (108), 5-(2-thiazolylazo)-salicylic acid (109), 2-[2-(3,5-dibromopyridylazo)-5-dimethylaminobenzoic acid (110) and 1-(2-quinolylazo)-2,4,5-trihydroxy benzene (111).
Present work:

Preliminary investigations on the colour reactions showed that the addition of TBT to a very dilute solution of iron (II) gave a dark red colour. This colour reaction was investigated in detail for microdetermination of iron (II) spectrophotometrically.

**EXPERIMENTAL**

**Iron (II) solution:**

A stock solution of iron (II) was prepared by dissolving an appropriate amount of ferrous ammonium sulphate hexahydrate (AnalaR) in acidulated double distilled water. The solution was standardized volumetrically with the help of potassium permanganate (53).

**Phosphate buffer, pH 6.0:**

A phosphate buffer (53) was prepared by diluting 250 ml of 0.2M potassium dihydrogen phosphate and 28.2 ml of 0.2M sodium hydroxide to 1 l with distilled water.

**Spectral behaviour of the complex and effect of pH:**

A series of solutions containing 1.0 ml of 2×10⁻³M iron (II) and excess of TBT (1.0 ml of 1×10⁻³M) was prepared and pH's were adjusted at different levels in a
total volume of 25 ml. The spectra of the solutions were recorded against the corresponding reagent blanks. Spectral studies revealed that only one complex was formed at all pH levels, absorbing maximum ($\lambda_{\text{max}}$) at 530 nm (fig. IV.6).

The absorbance values recorded at $\lambda_{\text{max}}$ 530 nm at different pH levels plotted against pH (fig. IV.7) showed that constant and maximum absorbance was exhibited in the pH range 5.3 - 6.8. In further investigations 2 ml of a phosphate buffer of pH ~ 6.0 was used which served the purpose to maintain the appropriate pH for complexation.

Effect of reagent concentration:

The absorbances of the colour developed of a series of solutions containing 1.0 ml of $2 \times 10^{-4}$ M iron (II), varying amounts of THT and 2.0 ml of phosphate buffer in a total volume of 25 ml were plotted against the concentration of the reagent (fig. IV.8) which showed that maximum colour was developed when THT concentration was kept more than 2 molar times the metal concentration. However, in further studies 10 times molar excess of THT was maintained.

Physico-chemical characteristics of the complex:

The results obtained for validity of Beer's law, optimum concentration, as evaluated by Rimgom plot (fig. IV.9), Sandell's sensitivity (for $\log I_0/I = 0.001$),
FIG. IV.6. ABSORPTION SPECTRA OF Fe(II) – THT COMPLEX AT DIFFERENT pH

Fe(II) = 8 \times 10^{-6} \text{ M}
THT = 4 \times 10^{-5} \text{ M}

FIG. IV.7. EFFECT OF pH ON Fe(II) – THT COMPLEX

Fe(II) = 8 \times 10^{-6} \text{ M}
THT = 4 \times 10^{-5} \text{ M}
**Fig. IV.8. Effect of Reagent Concentration on Fe(II)—THT Complex**

Fe(II) = $8 \times 10^{-6}$ M

**Fig. IV.9. Ringbom Plot for Fe(II)—THT Complex**

% Transmittance vs. Log ppm
molar extinction coefficient \((\varepsilon)\) of the colour reaction are summarized in table IV.4.

Table IV.4: Physico-chemical constants of the iron(II) - THT complex

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\lambda_{\text{max}})</td>
</tr>
<tr>
<td>2</td>
<td>Beer's law</td>
</tr>
<tr>
<td>3</td>
<td>Optimum concentration range</td>
</tr>
<tr>
<td>4</td>
<td>Sandell's sensitivity</td>
</tr>
<tr>
<td>5</td>
<td>Molar extinction coefficient ((\varepsilon))</td>
</tr>
<tr>
<td>6</td>
<td>Molar composition by Job's method (fig. IV.10)</td>
</tr>
</tbody>
</table>

**Recommended procedure:**

To a suitable aliquot containing 4-20 \(\mu g\) of iron add excess of THT solution (at least 5 molar times) followed by 2 ml of phosphate buffer (pH 6.0) and dilute to 25 ml with water. Measure the absorbance at 530 nm against a reagent blank prepared under similar conditions. Knowing the absorbance, iron content can be deduced from calibration curve.

**Absorbance deviations and accuracy of the method:**

The mean absorbance of a series of solutions containing 1 ml of \(2 \times 10^{-4}\text{M}\) of iron (II) and excess of THT in total
FIG. IV.10. COMPOSITION OF Fe(II)- THT COMPLEX BY JOB'S METHOD

TOTAL MOLARITY = 6 \times 10^{-5} \text{ M}

\[ \frac{[M]}{[M] + [R]} \]
volume of 25 ml at pH 6.0 was found to be 0.40, with a standard deviation of 0.0015.

The accuracy of the method was within the permissible limits which was checked by preparing a series of solutions containing different amounts of iron (II) (4-20 \( \mu \)g) and following the recommended procedure. The percentage error range was 0.21 - 1.8% for the ten solutions of this series.

Effect of diverse ions:

In the determination of iron(II) at the 0.56 \( \mu \)g/ml level, chloride, bromide, iodide, nitrate, nitrite, thiosulphate, sulphide, thiourea, thiosemicarbazide, tartrate, borate, phosphate, arsenate, alkaline earths, lanthanides, aluminium (III), chromium (III), copper (II), and platinum metals did not interfere at all. However, EDTA, cyanide, fluoride, zinc (II) and manganese (II) interfered seriously. Results of tolerance limits, in parts per million of various ions in solution that caused a deviation smaller than ±2% in absorbance, are given in table IV.5.

Table IV.5: Effect of diverse ions

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Tolerance limits (ppm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiocyanate</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Oxalate</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Citrate</td>
<td>120</td>
<td>-</td>
</tr>
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Acetylacetonate (acac.)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Amount</th>
<th>Masked by</th>
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<tbody>
<tr>
<td>Cadmium (II)</td>
<td>20</td>
<td>I⁻</td>
</tr>
<tr>
<td>Mercury (II)</td>
<td>30</td>
<td>I⁻</td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>5</td>
<td>acac</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>4</td>
<td>acac</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>10</td>
<td>S²O₃⁻³</td>
</tr>
<tr>
<td>Silver (I)</td>
<td>15</td>
<td>I⁻</td>
</tr>
<tr>
<td>Lead (II)</td>
<td>20</td>
<td>S²O₃⁻³</td>
</tr>
<tr>
<td>Indium (III)</td>
<td>25</td>
<td>S²⁻</td>
</tr>
<tr>
<td>Bismuth (III)</td>
<td>20</td>
<td>S²⁻</td>
</tr>
<tr>
<td>Antimony (III)</td>
<td>20</td>
<td>S²⁻</td>
</tr>
<tr>
<td>Thorium (IV)</td>
<td>40</td>
<td>PO₄³⁻</td>
</tr>
<tr>
<td>UO₂⁺⁻ (II)</td>
<td>8</td>
<td>AsO₄³⁻</td>
</tr>
</tbody>
</table>

Discussion:

Of the various methods known for the spectrophotometric determination of iron, thiocyanate method (1-3) in spite of its several disadvantages is widely used. It is because of its ready availability and cheapness. It reacts in a moderately acidic medium with ferric ions to yield a red colour, which for a long time, was the basis for the determination of iron (III), or total iron after oxidation of Fe(II) to Fe(III).
When iron is determined in aqueous media or in the presence of acetone, care should be taken that the concentration of thiocyanate is the same in the sample and the standard solutions. Iron (III) thiocyanate complexes are not very stable, and can persist only at a relatively high concentration of thiocyanate. Anions which form stable complexes with iron (III) (i.e. fluoride, phosphate, citrate and oxalate) interfere in the determination of iron by the thiocyanate method. High concentrations of chloride, sulphate and acetate also interfere, but to a lesser degree. Interference due to cobalt, molybdenum, bismuth and titanium is also caused due to formation of coloured thiocyanate complexes under the same conditions and by metals giving sparingly soluble thiocyanates.

Iron (II) or total iron can be determined with 1,10-phenanthroline or 2,2'-bipyridyl, after reducing iron (III) to iron (II)(1-3). The colour reactions are usually carried out in acetate or citrate buffers. The presence of acetate or citrate is desirable as it prevents the precipitation of certain cations which hydrolyse in weak acid media. Oxidation of iron (II)-phenanthroline complex yields a pale blue complex which can be used to determine relatively high concentrations of iron, but it is slowly converted into a stable yellow
complex with $\lambda_{\text{max}}$ 360 nm. A number of bivalent metals react with phenanthroline and bipyridyl to form colourless complexes which in the case of zinc and cadmium are more stable than iron (II) complex and should be masked. Copper also interferes and is masked by thioglycollic acid. Phosphate, oxalate and fluoride interfere if the pH of the solution is above 4.0.

Sulphosalicylic acid (2) forms a red violet complex with ferric ions at pH 2-3, a brown-orange complex at pH 4-7 and a yellow complex at pH 8-10. The violet complex which is stable in acid medium is more useful for the spectrophotometric determination of iron (III) in presence of iron (II), but the method has a poor sensitivity. More often, total iron [after oxidation of iron (II)] is determined as the yellow sulphosalicylate complex in alkaline medium but this method is also not very sensitive. Moreover, sulphosalicylate forms water-soluble complexes with most multivalent metal ions.

Schilt (57) has critically reviewed the ferroin type of reagents used for the determination of iron. Bathophenanthroline (53) is a highly sensitive and selective reagent but is quite expensive and difficult to synthesise. Copper interferes in the determination due to formation of a very stable and almost colourless complex between copper (I) and the reagent; needs prior separation. Higher concentrations of cobalt, nickel, zinc and cadmium also interfere.
3,3'-Bis(5,6-diphenyl-1,2,4-triazine) (67) and their sulphonated derivatives formed intensely coloured tris-chelate with iron (II) in molar acid solution and chelates were also formed with Cu(I) ions. The reagents showed an exceptionally high acid tolerance in its ability to chelate Fe(II) in concentrated acid. Only EDTA, CN⁻ and comparable amounts of Cu(I) and Co(II) interfered.

2,6-Bis(4-phenyl-2-pyridyl)-4-phenyl pyridine (61) is a sensitive ferroin type of reagent. However, several factors limit its use in practical applications, such as cost, difficulty of synthesis and solubility limitations.

Iron reacts with 2,2'-dipyridyl ketosaninomethylene (73) to form 1:2 complex. The complex has \( \lambda_{\text{max}} \) at 608 nm with \( \varepsilon = 17100 \, \text{dm}^3 \, \text{mol}^{-1} \, \text{cm}^{-1} \). Calibration curve was linear for 0.1 - 50 \( \mu \) g/ml. Iron (II) showed a variation coefficient of 0.57%.

However, Cr(III), Cu(II), Co(II), Cyanide and sulphide interfered.

Among the various oximes used for the purpose 2,2'-dipyridyl ketoamine (86) is the best suited for determination of iron in alkaline medium. 3-Hydroxy-2-methyl-1,4-naphthoquinone monoxime (89) is suggested by Kamini et al. for the spectrophotometric determination of iron(II). However, the reagent also forms complex with Co(II).
Among the various thiosemicarbazones used for determination of iron, bipyridyl glyoxal dithiosemicarbazone (93) has better sensitivity. However, alcohol concentration, type of oxidising agent used and pH have marked effect on complexation. The tolerance limits of various ions are also poor.

Several heterocyclic azo dyes have been used for the spectrophotometric determination of iron. 4-(2-Pyridylazo)-resorcinol (98,99) is a sensitive reagent. However, cobalt, copper and nickel interfere seriously. 1-(5'-Chloro-2',3'-dihydroxy pyridyl-4'-azo)benzene-1'-sulphonic acid (103) is a highly sensitive reagent, but palladium (II) and osmium (VIII) interfere seriously. Iron has also been determined in some synthetic solutions. Iron forms 1:2 complex with 5-(3,5-dibromo-2-pyridylazo)-2,4-diaminotoluene (106) at 556 nm with $\varepsilon = 4 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ and is very sensitive. But the tolerance limits of interfering ions are poor.

The present method, although, is not highly selective method, selectivity has been increased by making use of certain masking agents. Cadmium (II), mercury (II) and silver (I) have been masked with iodide and 9-fold concentrations of cobalt (II) and nickel (II) are masked by acetylacetone. Sulphide and thiosulphate have been used to mask indium (III), antimony (III), bismuth (III), lead (II) and copper (II). Phosphate and arsenate have been used to mask thorium (IV) and uranyl (II) respectively. Comparison of the sensitivities of certain well known methods with this method for the determination of iron shows that the present method is highly sensitive as well (Table IV.6).
<table>
<thead>
<tr>
<th>Reagent</th>
<th>Sensitivity (µg Fe(0)/cm²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiocyanate</td>
<td>0.008/480 nm</td>
<td>1-3</td>
</tr>
<tr>
<td>1,10-Phenanthroline</td>
<td>0.005/588 nm</td>
<td>1-3</td>
</tr>
<tr>
<td>2,2'-Dipyridyl</td>
<td>0.007/522 nm</td>
<td>1-3</td>
</tr>
<tr>
<td>Bathophenanthroline</td>
<td>0.002/533 nm</td>
<td>58</td>
</tr>
<tr>
<td>2,2'-Dipyridyl ketoxime</td>
<td>0.003/540 nm</td>
<td>86</td>
</tr>
<tr>
<td>2-Acetylpyrididine-4-phenyl-3-thiosemicarbazone</td>
<td>0.008/650 nm</td>
<td>92</td>
</tr>
<tr>
<td>Chromes axrol S in presence of cationic surfactant</td>
<td>0.00043/645 nm</td>
<td>82</td>
</tr>
<tr>
<td>Eriocyanine R in presence of cationic surfactant</td>
<td>0.00045/635 nm</td>
<td>82</td>
</tr>
<tr>
<td>1-(2-Pyrilylazo)-2-naphthonol</td>
<td>0.0035/550 nm</td>
<td>96</td>
</tr>
<tr>
<td>1-(5'-Chloro-2',3'-dihydroxy-4'-azo)benzene-4'-sulphonic acid)</td>
<td>0.0069/580 nm</td>
<td>103</td>
</tr>
<tr>
<td>1-(2-Quinolylazo)-2,4,5-trihydroxy benzene</td>
<td>0.003/510 nm</td>
<td>111</td>
</tr>
<tr>
<td>Tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt (THT)</td>
<td>0.0011/530 nm</td>
<td>Present method</td>
</tr>
</tbody>
</table>
C. COBALT

The principal oxidation states of cobalt are +2 and +3. Cobalt is present as Co(II) in practically all its simple compounds, whereas simple Co(III) compounds are almost non-existent. Cobalt (II) has a strong affinity for nitrogen donors and complexes of cobalt (II) with oxygen donors are less stable than those of nitrogen. On the other hand, cobalt (III) has a very strong tendency to form complex compounds; the most stable complexes are those in which cobalt is bonded with nitrogen, then carbon (in cyanides), oxygen, sulphur and halogens in order of decreasing stability.

Spectrophotometric reagents for cobalt (II):

A large number of reagents are known for the spectrophotometric determination of cobalt. Critical accounts of these reagents have been given in literature (1-3, 112-114). Compounds containing the nitrosohydroxyl chromophore, \[ \text{C (NO)} - \text{C (OH)} = \], are found to be specific for cobalt under set conditions. Some of the chromogenic reagents containing this grouping are:

- 1-nitroso-2-naphthol, 2-nitroso-1-naphthol and nitroso-R-salt (1-3),
- 2-nitroso-5-diethylaminophenol (115),
- 3-nitroso-2,6-pyridinediol (116),
- 3-nitroso-4-hydroxy-5,6-dibenzo-coumarin (117),
- 2-amino-5-nitroso-4,6-pyrimidinediol (118),
- 7-nitroso-8-hydroxyquinoline-5-sulphonic acid (119),
3-nitrososalicylic acid (120), 2-nitroso-1-naphthol-3-sulphonic acid (121) and 2,6-diamino-4-hydroxy-5-nitrosopyrimidine (122).

Among the thiosemicarbazones recently reviewed by Singh et al. (56), the most sensitive ones are: picolinaldehyde-phenyl-3-thiosemicarbazone (123), 1,3-cyclohexanedione dithiosemicarbazone (124) and salicylaldehyde thiosemicarbazone (125). Some of the promising oximes reviewed by Singh et al. (55) are: 2,2'-diquinolylketoxime (126), dimesonedioxime (127), benzimidazol-2-carboxanilide oxime (128), 2-pyridyl-2-thienyl-β-ketoxime (129), biacetyl monoxime-2-pyridyldihydrazone (130), 3-hydroxy-2-methyl-1,4-naphthaquinone monoxime (131) and 2-hydroxy-1-naphthaldoxime (132).

Some other important reagents known for cobalt are dithioxamide (133), quinoxaline-2,3-dithiol (134), thiocyanate (135), thioulorubic acid (136), 2-thenyltrifluoroacetone (137), thiotropolone (138), 2,2'-dipyridyl-2-pyrimidyl hydrazone (139), 2,2'-pyridyl-bis (2-quinolylhydrazone) (140), 4-(6-chlorindazol-3-ylazo)-3-hydroxy-naphthalene-2,7-disulphonic acid (141), biacetyl mono-(2-pyridyl hydrazone) (142), 3-(2-acetylphenyl)-1-methyltriazine-N-oxide (143), 3-bromo-2-hydroxy-5-methylacetophenone hydrazone (144), 1,2-diaminocyclohexanetetraacetate (145), 1,3-bis [(2-pyridyl)methyleneamino] thiourea and 1,3-bis [(2-pyridyl)methyleneamino] guanidine (146),
In recent years there has been a remarkable growth in the number of highly sensitive methods for determining cobalt based on complexation with azo compounds. Numerous heterocyclic azo dyes have been employed for the purpose, a few of which are: 1-(2-pyridylazo)-2-naphthol (157), 4-(2-pyridylazo)resorcinol (157), 5-(ethylamino)-2-(2-pyridylazo)-p-cresol and its halo derivatives (158), 1-(5-chloro-2', 3'-dihydroxypyridyl-4'-azo)benzene-4-sulphonic acid (103), 5-(3,5-dichloro-2-pyridylazo)-2,4-diaminotoluene (159), 4-[5-chloro-2-pyridylazo]-1,3-diaminobenzene (160), 4-(2-pyridylazo)-4'-phenylenediamine (161), 5-(2-pyridylazo)-2,4-diaminotoluene and their halo derivatives (162), diamino-(pyridylazo)benzene and its derivatives (163), 1-(2-pyridylazo)-phenanthrene-2-ol (164), 1-(2-thiazolylazo)-naphthol and 4-(2-thiazolylazo)resorcinol (165), 1-(2-quinolylazo)-2-acenaphthylol (166), 1-(2-lepidylazo)-2-acenaphthylol (167), 2-[2-(3,5-dibromopyridylazo)]-5-dimethylamino benzoic acid (168), 9-(2-pyridylazo)-10-phenanthrol
115

(169), 4-[(5-chloro-2-pyridyl)azo]-1,3-diaminobenzene (170), 5-(3,5-dibromo-2-pyridylazo)-2,4-diaminotoluene (171), 2,2'-dipyridyli-2-benzothiazolylhydrazone (172), 1-amino-7-(3-quinolylazo)-8-hydroxynaphthalene-3,6-disulphonic acid and 2-(8-quinolylazo)-7-phenylazo-1,6-dihydroxy naphthalene-3,6-disulphonic acid or 2-(8-quinolylazo)-7-phenylazochromotropic acid (173) and 1-(8-quinolylazo)-2,4,5-trihydroxybenzene (111).

**Present work:**

Cobalt (II) forms a dark brown coloured complex with an aqueous solution of tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt (THT). Spectrophotometric investigations on the complexation have been made in detail as under.

**Experimental**

**Stock solution of cobalt (II):**

A stock solution of cobalt (II) was prepared by dissolving cobalt sulphate heptahydrate (AnalaR, BDH) in double distilled water and it was standardized gravimetrically, weighing as anthramilate (53).

**Acetate buffer, pH 5.0:**

An acetate buffer (53) solution was prepared by making up 300 ml of 0.2N acetic acid to 1 l with 0.2N sodium acetate solution.
Dilute solutions of sodium hydroxide and hydrochloric acid were also used for pH adjustment.

**Spectral characteristics of the complex and effect of pH**

A series of solutions containing 1.0 ml of $2 \times 10^{-4} M$ cobalt solution and sufficient excess of THT (1.0 ml of $1 \times 10^{-3} M$) was prepared and pH's were adjusted at different levels. The solutions were diluted to 25 ml with distilled water. The spectra of the solutions, recorded against corresponding reagent blanks, show that only one complex ($\lambda_{\text{max}}$ at 500 nm) is formed at all pH levels (fig. IV.11).

Plot of pH vs. absorbance at the $\lambda_{\text{max}}$ shows that constant and maximum absorbance is exhibited in the pH range 4.5 - 6.5 (fig. IV.12). Subsequent studies, have been carried out in acetate buffer of pH 5.0.

**Effect of reagent concentration**

Absorbance of the solutions containing variable amounts of the reagent and fixed amount of cobalt (II) at pH 5.0, against the corresponding reagent blanks showed that at least 4-times molar excess of THT (fig. IV.13) is required for full colour development. However, in further investigations 10 times molar excess of the reagent has been used.
Fig. IV.11. Absorption spectra of Co(II) - THT complex at different pH

Co(II) = 8 x 10^{-6} M
THT = 4 x 10^{-5} M

Fig. IV.12. Effect of pH on Co(II) - THT complex

Co(II) = 8 x 10^{-6} M
THT = 4 x 10^{-5} M
Physico-chemical characteristics of the complex

The results obtained for validity of Beer's law along with optimum concentration range, obtained from Ringbom plot (fig. IV.14), sensitivity and molar extinction coefficient of the complex at pH 5.0 are recorded in table IV.7.

Table IV.7: Physico-chemical constants of the cobalt (II) - THT complex

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\lambda_{\text{max}}$</td>
<td>500 nm</td>
</tr>
<tr>
<td>2</td>
<td>Beer's law range</td>
<td>0.0 - 1.30 ppm</td>
</tr>
<tr>
<td>3</td>
<td>Optimum concentration range</td>
<td>0.15 - 1.10 ppm</td>
</tr>
<tr>
<td>4</td>
<td>Sandell's sensitivity</td>
<td>0.0016 ($\mu$g Co(II)/cm$^2$)</td>
</tr>
<tr>
<td>5</td>
<td>Molar extinction coefficient ($\varepsilon$)</td>
<td>$3.7 \times 10^4$ l.mol$^{-1}$.cm$^{-1}$</td>
</tr>
<tr>
<td>6</td>
<td>Molar composition by Job's method (fig. IV.15)</td>
<td>1:2 (MsL)</td>
</tr>
</tbody>
</table>

Recommended procedure:

To a suitable aliquot of cobalt (II) solution containing 3.7-27.5 $\mu$g is added sufficient excess of THT solution followed by 1.0 ml of acetate buffer (pH 5.0) and diluted to 25 ml with distilled water. The absorbance is recorded at 500 nm against the corresponding reagent.
**Fig. IV.13. Effect of Reagent Concentration on Co(II) - THT Complex**

**Fig. IV.14. Ringbom Plot for Co(II) - THT Complex**

Co(II) = $8 \times 10^{-6}$ M
FIG. IV.15. COMPOSITION OF Co(II) - THT COMPLEX BY JOB'S METHOD

TOTAL MOLARITY

= 6 \times 10^{-5} \text{ M}
blank, prepared under identical conditions. The amount of the cobalt present in the unknown solution is deduced from the calibration curve.

**Absorbance deviations and accuracy of the method:**

The mean absorbance of a series of ten solutions containing 1 ml of $2 \times 10^{-6}$ M of cobalt (II) and excess of THT in total volume of 25 ml at pH 5.0 was found to be 0.295, with a standard deviation of 0.0008.

The percentage error of the results for determining cobalt (II) following the recommended procedure of a series of ten solutions containing 3.7 to 27.5 $\mu$g cobalt (II) was in the range 0.25 - 2.1%, which showed the fair accuracy of the method.

**Effect of diverse ions:**

In the determination of cobalt (II) at the 0.59 $\mu$g/ml level, fluoride, chloride, bromide, iodide, nitrite, nitrate, thiocyanate, citrate, tartrate, oxalate, sulphide, thiourea, borate, phosphate, alkaline earths, lanthanides, aluminium (III), chromium (III), and platinum metals did not interfere at all. However, EDTA, cyanide, acetylacetone, zinc (II) and manganese (II) interfered seriously while 3-fold excess of nickel was tolerated, as nickel complex had a little absorbance (~ 1%) at 500 nm at this concentration. Results of tolerance limits, in parts
per million of various ions in solution that caused a deviation smaller than ±2% in absorbance are given in table IV.8.

Table IV.8: Effect of diverse ions

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Amount tolerated (ppm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea semicarbazide</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>Arsenate</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Cadmium (II)</td>
<td>10</td>
<td>masked by I⁻</td>
</tr>
</tbody>
</table>
| Mercury (II)          | 12                     | masked by I⁻ or  
|                       |                        | arsenate⁻ 3     |
| Iron (II)             | 5                      | masked by F⁻    |
| Copper (II)           | 15                     | masked by  
|                       |                        | arsenate⁻ 3     |
| Silver (I)            | 8                      | masked by I⁻    |
| Lead (II)             | 20                     | masked by  
|                       |                        | arsenate⁻ 3     |
| Indium (III)          | 15                     | masked by  
|                       |                        | arsenate⁻ 3     |
| Bismuth (III)         | 10                     | masked by  
|                       |                        | arsenate⁻ 3     |
| Antimony (III)        | 15                     | masked by  
|                       |                        | arsenate⁻ 3     |
| Thorium (IV)          | 30                     | masked by  
|                       |                        | PO₄²⁻            |
| Uranyl (II)           | 7                      | masked by  
|                       |                        | AsO₃²⁻           |

Discussion:

The reagents containing the nitroso-hydroxyl grouping = C (NO) - C (OH) = are well known for the spectrophotometric determination of cobalt. Trivalent cobalt generally reacts...
with compounds containing this chromophore which also serve as oxidising agents. The peculiarity of this grouping is that it reacts quantitatively with cobalt (II) only in weakly acidic or neutral solutions. But once formed the chelate is not appreciably dissociated even by strong acids. This behaviour of the cobalt chelate has been utilised in its determination in presence of nickel, copper or iron etc., whose chelates are easily dissociated. 

Nitroso-R-salt (3) is a well known compound of this class. Sensitivity of the method is an advantage in addition to its selectivity, as large quantities of foreign ions do not interfere. Nitrosophenols (3) are also used for the purpose, but excess of the reagents interferes in the determination.

3-Nitrososalicylic acid (120) has been used for determination of small quantities of cobalt. Nickel also forms a red complex with the reagent, but the brown cobalt complex can be extracted in petroleum ether, leaving the nickel complex in aqueous phase. The method is applicable for simultaneous determination of cobalt and nickel. But copper and iron interfere appreciably in the determination.

2,6-Diamino-4-hydroxy-5-nitrosopyrimidine (122) is a sensitive spectrophotometric reagent for cobalt. But in this method lead (II), bismuth (III), iron (II), aluminium (III) and barium (II) interfere in concentration of 2 ppm and silver (I), mercury (II), copper (II), tin (II) and
Picolinaldehde-4-phenyl-3-thiosemicarbazone (123) is one of the sensitive thiosemicarbazones used. It gives different complexes in weakly and highly acidic media, but tolerance limits are very poor.

2,2'-(Alquinolyl)ketoxime (126) is the most promising among the oximes which react with cobalt in highly alkaline medium. The method is made selective by extraction of several cations. However, Mg(II), Mn(II), Cr(III), Ir(III), Rh(III), Ru(III), Os(III), Ce(III), Ta(V), tartrate, cyanide and EDTA interfere seriously.

3-Hydroxy-2-methyl-1,4-naphthaquinone monoxime (131) is suggested for the spectrophotometric determination of cobalt (II). The determination is carried out in 50% ethyl alcohol. But Fe(II) also forms complex with the reagent.

Cobalt (II) reacts with 2-hydroxy-1-naphthaldoxime (132) to form a water insoluble complex in aqueous solution at pH 8.3 - 9.2 which can be extracted quantitatively into ethylacetate. The complex is stable and has the sensitivity $5.1 \times 10^{-3} \mu g/Co/cm^2$ at 387 nm. However, Cu(II), Fe(III), and Ni(II) interfere seriously.

Concentrated solution of thiocyanate produces a blue colour with cobaltous ions which fades when the solution is diluted with water, owing to dissociation of the complex. However, acetone or any other water-miscible organic solvent
suppresses the dissociation of the complex and restores the blue colour of \([\text{Co(SCN)}_4]^{2-}\) species. Since iron (III) also forms coloured complex with thiocyanate and thus interferes strongly. Interfering elements include other metals also which form coloured thiocyanate complexes e.g., V, Bi, U, Cu, Mo and W, and the metals which give precipitates e.g., Ag, Tl(I), Cu(I).

Maleonitriledithiolate (153) forms brown complex with cobalt (II) at 460 nm with \(\varepsilon = 5.01 \times 10^3\ \text{l.mol}^{-1}.\text{cm}^{-1}\). Cu(II), Ni(II), Mo(VI), V(VI), Pd(II) and Pt(IV) interfere in the determination.

1,2-Diaminocyclohexanetetracetate (DCTA) (145) forms complex with cobalt (II). The photochemical oxidation of \([\text{Co(DCTA)}]^-\) by reagent in the presence of \(\text{H}_2\text{DCTA}^{2-}\) was utilised as spectrophotometric determination of cobalt(II) at 540 nm. Nitrite inhibits the photochemical formation of \([\text{Co(DCTA)}]^-\). Mn(II), Cr(III), Fe(III), Ni(II) and Cu(II) also interfere.

2-Thiophene-carboxaldehyde-2-quinolylhydrazide (152) reacts stoichiometrically with cobalt (II) in strong alkaline medium at 375-395 nm. However, Palladium also forms 1:1 complex at 375-395 nm.

In recent years remarkable number of heterocyclic azo dyes have been used for the determination of cobalt, but only a few have been found for practical use. PAN forms a red complex with cobalt (II), which gradually changes to green (157).
Oxidation of the complex is prevented by the presence of some reducing agents. The complex can be extracted into chloroform at pH 4.7. PAR (157) forms a red complex which is water soluble but it needs heating at 70-80° for 30 minutes for full colour development.

5-(3,5-Dibromo-2-pyridylazo)-2,4-diaminotoluene (171) is a suitable colouring reagent which forms a stable coloured complex absorbing at 540 and 580 nm at pH 5.5-7.7. In the presence of citric acid, most of the elements do not interfere with the cobalt (II) determination and iron as much as 1 mg/ml can be tolerated. NO₃ interferes with the cobalt determination and NO₃ destroys the reagent.

The present method is very simple method and it does not need any heating as in case of PAR or presence of any reducing agent to prevent oxidation as in case of PAN. However, the method is not very selective and attempts are made to mask certain base metals which interfere. Cadmium (II), mercury (II) and silver (I) have been masked by iodide, iron (II) by fluoride, lead (II) and copper (II) by thiosulphate and iridium (III), bismuth (III) and antimony (III) by making use of sulphide. Phosphate and arsenate have been used to mask thorium (IV) and uranyl (II) ions respectively. Sensitivity of the method is also well comparable with well known methods. A comparison of sensitivities of important methods has been presented in table IV.9.
<table>
<thead>
<tr>
<th>Reagents</th>
<th>Molar absorptivities at $\lambda_{\text{max}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitro so-R-salt</td>
<td>$3.1 \times 10^4 / 420$ nm</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>$1.4 \times 10^4 / 520$ nm</td>
<td>3</td>
</tr>
<tr>
<td>Nitro so-1-naphthol/CHCl$_3$</td>
<td>$1.4 \times 10^4 / 530$ nm</td>
<td>3</td>
</tr>
<tr>
<td>2-Nitro so-5-dimethylamino-phenol</td>
<td>$6.0 \times 10^4 / 456$ nm</td>
<td>115</td>
</tr>
<tr>
<td>2-Amino-5-nitro so-4,6-pyrimidinediol</td>
<td>$7.85 \times 10^4 / 360$ nm</td>
<td>118</td>
</tr>
<tr>
<td>Thiovioluric acid</td>
<td>$5.9 \times 10^4 / 425$ nm</td>
<td>136</td>
</tr>
<tr>
<td>1-(2-Pyridylazo)-2-naphthol/CHCl$_3$</td>
<td>$2.7 \times 10^4 / 550$ nm</td>
<td>157</td>
</tr>
<tr>
<td>1-(2-Pyridylazo)resorcinol (PAR)</td>
<td>$5.6 \times 10^4 / 510$ nm</td>
<td>157</td>
</tr>
<tr>
<td>5-(Ethylamino)-2-(2-pyridylazo)-p-cresol (CAPAC)</td>
<td>$7.4 \times 10^4 / 530$ nm</td>
<td>158</td>
</tr>
<tr>
<td>4-(2-Thiazolylazo)resorcinol</td>
<td>$2.5 \times 10^4 / 570$ nm</td>
<td>165</td>
</tr>
<tr>
<td>1-(2-Thiazolylazo)-naphthol</td>
<td>$3.7 \times 10^4 / 570$ nm</td>
<td>165</td>
</tr>
<tr>
<td>1-(2-Quinolylazo)-2-acenaphthyleneol (CAAC)/CCl$_4$</td>
<td>$5.4 \times 10^4 / 550$ nm</td>
<td>166</td>
</tr>
<tr>
<td>1-(2-Lepidylazo)-2-acenaphthyleneol (LAAC)/CCl$_4$</td>
<td>$5.62 \times 10^4 / 550$ nm</td>
<td>167</td>
</tr>
<tr>
<td>1-(2-Quinolylazo)-2,4,5-trihydroxybenzene</td>
<td>$1.3 \times 10^4 / 500$ nm</td>
<td>111</td>
</tr>
<tr>
<td>Tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt (THT)</td>
<td>$3.7 \times 10^4 / 500$ nm</td>
<td>Present method</td>
</tr>
</tbody>
</table>
D. NICKEL

Nickel with $3d^8\,4s^2$ electronic configuration, is generally encountered in its compounds in the oxidation state $+2$, some hydrated oxides of $\text{M(III)}$ and $\text{M(IV)}$ are exceptions. Though the formal oxidation state of nickel in its complexes may range from 0 to $+4$, the commonest central ion is $\text{M(II)}$. The $\text{M(II)}$ complexes with coordination number six are octahedral, while the coordination number four is less common and have tetrahedral and square-planar geometries.

Spectrophotometric reagents for nickel:

Various reagents known for the spectrophotometric determination of nickel have been reviewed by various workers (1-3, 55, 174). Although few inorganic reagents are also known, the organic reagents have been found to be more sensitive.

Vicinal-dioximes (174) are known to be the ideal reagents amongst the various classes of organic compounds. 4-Isopropyl-1,2-cyclohexanedionedioxime (175) was proposed as an excellent reagent, but dimethylglyoxime ($\text{DGO}$)(176-178) is the best known of all the reagents in this class.

Various oximes used for spectrophotometric determination of nickel have been recently reviewed by Singh et al. (55). Some of the sensitive ones are:
cyclohexane-1,2-dione dioxime (179), cyclohexane-1,2,3-trione trioxime (180), benzil-α-dioxime (181), furil-α-dioxime (182), cycloheptane-1,2-dione dioxime (183), oxamideoxime (184), resacetophenone oxime (185), 4-t-butylcyclohexane-1,2-dione dioxime (186), phenanthraquinone monoxime (187), 3-hydroxy-2-methyl-1,4-naphthoquinone monoxime (188), 3,5-dichloro-2-hydroxy acetophenone oxime (189), 3,5-dibromo-2,4-dihydroxy acetophenone oxime (190) and phenanthrenequinone monoxime (191).

Some other reagents proposed for the purpose are quinoxaline-2,3-dithiol (192), dithio-oxamide (193), thiotropolone (194), thiovioluric acid (195), 2,4-dihydroxythiobenzoic acid (196), pyridine-2-aldehyde-2-quinolylhydrazone (197), furcin thiosemicarbazone (198), p-arisaldehyde thiosemicarbazone (199), dithione and methyltriocetylammonium chloride (200), 3-methoxy-7-methylphenothiazine (201), 2-carboxy-2'-hydroxy-3’,5’-dimethylazo-benzene-4-sulphonic acid (202), 2,2’-bis pyridyl-2-quinolylhydrazone (203), 3-(o-acetophenyl)-1-methyltriazine-5-oxide (204), 1,3-cyclohexanedione bis thiosemicarbazone monohydrochloride (205), isonitrosothiocamphor (206), rubesanic acid (207), bis-(4-phenyl-3-thiosemicarbazone)(208), hydrazino carbotioamide-2-(2-furanyl methylene)(209), o-mercaptopacetooacetanilide (210), morpholine-4-carbodithiolate (211), cyclohexylideneammonium-2-aminocyclohexylidene-1-cyclohexane-1-dithiocarboxylate (212) and 3-(4-methoxyphenyl)-2-mercaptopropenoic acid (213).
Among the heterocyclic azo dyes the important ones are: 1-(2-pyridylazo)-2-naphthol (214, 215), 4-(2-pyridylazo)resorcinol (216), 1-(2-thiazolylazo)-2-naphthol (217), 1-(5-amino-1,3,4-thiazolylazo)-2-naphthol (218), 2-(2-thiazolylazo)-5-dimethylaminophenol (219), pyridyl-2-azo chromotropic acid (220), thiazolylazo cresol (221), 2-(2-thiazolylazo)-5-dimethylaminophenol, triton x-100 (222), 1-(5'-chloro-2',3'-dihydroxypyridyl-4'-azo)-benzene-4-sulphonic acid (103), 1-(2-benzothiazolylazo)phenanthrene-9-ol and triton x-100 (223), 2-[2-(3,5-dibromopyridylazo)]-5-dimethylaminobenzoic acid (224), 2-(2-thiazolylazo), 2-(2-benzothiazolylazo)-5-dimethyl aminobenzoic acid (225), 7-(4,5-dimethylthiazolyl-2-azo)-8-hydroxyquinoline-5-sulphonic acid (226), [5-(3,5-dichloro-2-pyridylazo)-2,4-diaminotoluene] (227), 6-(5-methyl-1,3,4-thiadiazol-2-ylazo)-3,4-dimethylphenol (228), 2-(5'-methyl-3'-isoxazoles)-4-methylenophenol (229), 2-phenolazoimidazole (230), 2-(4-antipyrylazo)-4-methyl-5-ethylaminophenol and 2-(4-antipyrylazo)-5-diethylaminophenol (231), di-2-pyridylmethane-2-benzothiazolylhydrazone (232) and 1-(2-quinolylazo)-2,4,5-tri-hydroxybenzene (111).

**Present work**

Nickel (II) forms a wine red coloured complex with THT in aqueous medium at neutral pH. This colour reaction has been investigated in detail with a view to ascertain potentiality of THT for spectrophotometric determination of nickel.
EXPERIMENTAL

M(II) solution:

A stock solution of nickel (II) was prepared by dissolving appropriate amount of nickel ammonium sulphate (Analar) in acidulated double distilled water. The solution was standardised gravimetrically (53).

Phosphate buffer, pH 7.0:

A phosphate buffer (53) solution was prepared by diluting a mixture of 250 ml of 0.2M potassium dihydrogen phosphate and 148 ml of 0.2M sodium hydroxide to 1 l with distilled water.

Spectral behaviour of the complex and effect of pH:

A series of solutions containing 1.0 ml of $2 \times 10^{-4}$ M nickel (II) and excess of THT (1.0 ml of $1 \times 10^{-3}$ M) was prepared and pH's were adjusted at different levels in a total volume of 25 ml. The spectra of the solutions were recorded against corresponding reagent blanks. Spectral studies showed that only one complex was formed which absorbed maximum at 570 nm at all pH values (fig. IV.16).

Plot of pH vs. absorbance at $\lambda_{\text{max}}$ (570 nm) showed that constant and maximum absorbance was exhibited in the pH range 6.6 - 7.3 (fig. IV.17). Subsequent studies were carried out in a phosphate buffer of pH 7.0 at the $\lambda_{\text{max}}$. For this purpose 2.0 ml of phosphate buffer was used.
FIG. IV. 16. ABSORPTION SPECTRA OF Ni(II) - THT COMPLEX AT DIFFERENT pH

6.6 - 7.3  \[ \text{Ni(II)} = 8 \times 10^{-6} \text{M} \]

6.3 - 7.8  \[ \text{THT} = 4 \times 10^{-5} \text{M} \]

5.4 - 9.0

WAVELENGTH (nm)

FIG. IV. 17. EFFECT OF pH ON Ni(II) - THT COMPLEX

Ni(II) = 8 \times 10^{-6} \text{M}

THT = 4 \times 10^{-5} \text{M}

pH

ABSORBANCE

FIG. IV. 17. EFFECT OF pH ON Ni(II) - THT COMPLEX
**Effect of reagent concentration**

Study of the effect of reagent concentration on complexation reaction showed that for maximum complexation, 3 times molar excess of THT was sufficient (fig. IV.18). However, for further studies, at least 5 times molar excess of THT was maintained.

**Physico-chemical characteristics of the complex**

The results obtained for validity of Beer's law, optimum concentration range, as evaluated by Ringbom plot (fig. IV.19), sensitivity and molar extinction coefficient of the colour reaction are summarised in table IV.10.

**Table IV.10 : Characteristics of the nickel(II)-(THT) complex**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>λ max</td>
</tr>
<tr>
<td>2.</td>
<td>Beer's law range</td>
</tr>
<tr>
<td>3.</td>
<td>Optimum concentration range</td>
</tr>
<tr>
<td>4.</td>
<td>Sandell's sensitivity</td>
</tr>
<tr>
<td>5.</td>
<td>Molar extinction coefficient (ε)</td>
</tr>
<tr>
<td>6.</td>
<td>Molar composition (fig. IV.20)</td>
</tr>
</tbody>
</table>
**FIG. IV. 18. EFFECT OF REAGENT CONCENTRATION ON Ni(II)-THT COMPLEX**

**FIG. IV. 19. RINGBOM PLOT FOR Ni(II)-THT COMPLEX**
FIG. IV. 20. COMPOSITION OF Ni(II) - THT COMPLEX
BY JOB'S METHOD

TOTAL MOLARITY
= 6 \times 10^5 M
Recommended procedure:

To a suitable aliquot containing 4.5 - 27.5 μg of nickel add 5 ml of 5x10^-5 M TBT solution followed by 2.0 ml of phosphate buffer and diluted to 25 ml with distilled water. Measure the absorbance at 570 nm against a reagent blank prepared under similar conditions. Knowing the absorbance, nickel content in the unknown solution can be deduced from the calibration curve drawn under similar conditions.

Absorbance deviations and accuracy of the method:

The mean absorbance of a series of eight solutions containing 2x10^-4 M of nickel (II) and excess of THT in total volume of 25 ml at pH 7.0 was found to be 0.335, with a standard deviation of 0.0037.

The accuracy of the method was checked by preparing a series of ten solutions containing different amounts of nickel (II) (4.5 - 27.5 μg) and fixed and excess amount of THT following the recommended procedure. The percentage error of the results of this series was in the range 0.22-1.8% which showed the accuracy of the method was within permissible limits accepted for spectrophotometric determinations.

Effect of diverse ions:

Effect of diverse ions was studied by preparing synthetic solutions containing 0.59 ppm of nickel (II) and
varying amounts of diverse ions and determining the nickel contents following the recommended procedure. Chloride, bromide, iodide, nitrate, nitrite, thiosulphate, sulphite, sulphide, thiocyanate, tartrate, borate, thiourea, phosphate, arsenate, alkaline earths, lanthanides, aluminium (III), vanadium (V), chromium (III), molybdenum (VI), tungsten (VI) and platinum metals did not interfere at all. However, cyanide, EDTA, and acetyl-cetone interfered. Two fold excess of manganese (II) or zinc (II) and equal amounts of cobalt (II) did not interfere, as the complexes of these metals at these concentrations did not show any absorbance at 570 nm. Results of tolerance limits, in parts per million of other ions in solution that caused a deviation smaller than ±2% in absorbance, are given in Table IV.11.

Table IV.11: Effect of diverse ions

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Tolerance limits (ppm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>Citrate</td>
<td>500</td>
<td>-</td>
</tr>
<tr>
<td>Oxalate</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td>Thiosemicarbazide</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td>Cadmium (II)</td>
<td>8</td>
<td>masked by I⁻</td>
</tr>
<tr>
<td>Mercury (II)</td>
<td>8</td>
<td>masked by I⁻ or S²O³⁻</td>
</tr>
<tr>
<td>Iron (II)</td>
<td>5</td>
<td>masked by F⁻</td>
</tr>
</tbody>
</table>
**Copper (II)** 15 masked by $S_2O_3^{2-}$  
**Silver (I)** 11 masked by $I^-$  
**Lead (II)** 15 masked by $S_2O_3^{2-}$  
**Indium (III)** 15 masked by $S^{2-}$  
**Bismuth (III)** 25 masked by $S^{2-}$  
**Antimony (III)** 25 masked by $PO_4^{3-}$  
**Thorium (IV)** 20 masked by $AsO_4^{3-}$  
**UO_2(II)** 5 masked by $AsO_4^{3-}$

**Discussion:**

Vicinal dioximes, which contain the $\text{HO}^+\text{C}=(\text{C}=\text{O})\text{H}$ grouping, react selectively with Ni(II). The nickel (II) complexes of these dioximes can be extracted into water immiscible organic solvents. The chelating agents of this class which are generally used for the purpose are dimethylglyoxime (DMG) (176-178) and furil-α-dioxime (182). DMG forms a wine red or brown colour when added to basic solution of a nickel salt which has been treated with an oxidizing agent. Two complexes having metal to DMG ratio of 1:2 and 1:4 are formed. The 1:4 complex is more stable and can be derived from the 1:2 complex by oxidation above pH 11.0. Its structure, however, has not been established. The colour development in the case of 1:4 complex is rather slow and requires heating at 60-70° for five minutes. DMG, if used alone, gives the 1:2 complex with nickel (II),
extractable in chloroform. The sensitivity is very low and maximum absorption takes place in the UV region.

Furil-α-dioxime (182) has been found to be more sensitive. But the disadvantage in this case is that the presence of alkali metal salts in concentrations greater than 0.1M, retard the extraction of the complex and extraction is not completed even on prolonged shaking.

3,5-Dichloro-2-hydroxyacetophenone oxime (189) forms a 1:2 complex with nickel (II) at pH 5.0-8.0 into isobutylmethyl ketone at 600 nm. However, copper also forms a 1:2 complex with the reagent at pH 3.0-8.5 at 640 nm.

Quinoxaline-2,3-dithiol (192) is a useful spectrophotometric reagent for nickel and it has also been recommended for the simultaneous determination of nickel and cobalt.

Pyridine-2-aldehyde-2-quinolylhydrazone (197) becomes selective in presence of thioglycolic acid. However, there is a need for strict pH control and the tolerance limits for anions are poor. Nickel forms 1:2 water-insoluble complex with di-2-pyridinylmethaneone-2-benzothiazolylhydrazone (232), which can be quantitatively extracted into benzene from aqueous medium of pH 4.0-10.3.

PAN (214, 215) forms a red complex with Ni(II) at pH 5-9 extractable in chloroform. Heating is required on a boiling water bath for about five minutes. There is
Interference from cadmium, manganese and zinc above pH 4.0. Cobalt (II) can be masked by cyanide and oxidized with hydrogen peroxide to form \( [\text{Co(CN)}_6]^{3-} \), which does not react with PAN. Shibata and coworkers (215) reported simultaneous determination of manganese and nickel. Manganese forms a complex in alkaline solutions only. PAR (216) also forms a complex with nickel, but heating is required to complete the complexation reaction.

1-(2-Quinolylazo)-2-acenaphthylenol (166) is another sensitive heterocyclic azo dye for determination of nickel. The reagent, however, is not selective and 125 molar excess of the reagent is needed for full colour development. 1-(2-Quinolylazo)-2,4,5-trihydroxybenzene (111) is a sensitive reagent for spectrophotometric determination of nickel. No heating is required as in case of PAR and PAR. However, the method is not selective.

2-Phenolazolimidazole (230) forms a stable complex with nickel (II) in 1:1 solution of water and dioxane. Co(II), Ni(II), Cu(II), Fe(II) and Fe(III) ions also form stable complexes with this. However, CN\(^-\), EDTA, Hg(II), Sn(II) and Mn(II) interfered.

The present azo dye is a highly sensitive reagent for the spectrophotometric determination of nickel(II), a comparison of sensitivities of various important methods has been shown in table IV.12. However, the method is not very selective, but selectivity has been increased by making use of masking agents. For example, cadmium(II), mercury(II), silver(I) are masked by iodide; iron(II) by fluoride;
copper (II) and lead by thiosulphate and indium(III), bismuth (III) and antimony (III) by sulphide. Zinc(II), cobalt(II) and manganese (II) interfere when present more than two fold excess and attempts to mask higher concentration have been failed, but the complexes formed by these metals with THT do not absorb at 570 nm, therefore, equal amount of cobalt (II) and 2-fold excess of manganese (II) or zinc (II) are tolerated in the determination of nickel (II).

Table IV.12: Sensitivities of some important reagents for nickel

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Sensitivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylglyoxime + oxidizing agent</td>
<td>0.0042/445 nm</td>
<td>176-78</td>
</tr>
<tr>
<td>Dimethylglyoxime/CHCl₃</td>
<td>0.017/375 nm</td>
<td>176-78</td>
</tr>
<tr>
<td>Furil-α-dioxime/CHCl₃</td>
<td>0.004/335 nm</td>
<td>182</td>
</tr>
<tr>
<td>Quinoxaline-2,3-dithiol</td>
<td>0.0034/656 nm</td>
<td>192</td>
</tr>
<tr>
<td>Dithio-oxamide</td>
<td>0.0046/640 nm</td>
<td>193</td>
</tr>
<tr>
<td>Thiovioluric acid</td>
<td>0.0025/375 nm</td>
<td>195</td>
</tr>
<tr>
<td>Pyridine-2-aldehyde-2-quinolylhydrazone</td>
<td>0.0011/492 nm</td>
<td>197</td>
</tr>
<tr>
<td>Furin thiosemicarbazone/CHCl₃</td>
<td>0.0038/410 nm</td>
<td>198</td>
</tr>
<tr>
<td>1-(2-Pyridylazo)-2-naphthol</td>
<td>0.0012/570 nm</td>
<td>214,215</td>
</tr>
<tr>
<td>4-(2-Pyridylazo)resorcinol</td>
<td>0.008/94 nm</td>
<td>216</td>
</tr>
<tr>
<td>1-(2-Quinolylazo)-2-acenaphthylenol</td>
<td>0.0013/560 nm</td>
<td>166</td>
</tr>
<tr>
<td>1-(2-Quinolylazo)-2,4,5-trihydroxybenzene</td>
<td>0.0011/540 nm</td>
<td>111</td>
</tr>
<tr>
<td>Tris-[2,4,6-(2-hydroxy-4-sulfo-1-naphthylazo)]-s-triazine, trisodium salt (THT)</td>
<td>0.0014/570 nm</td>
<td>Present method</td>
</tr>
</tbody>
</table>
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