CHAPTER VI

SPECTROPHOTOMETRIC DETERMINATION OF BISMUTH, INDIUM
AND ANTIMONY

A. BISMUTH

Bismuth occurs in its compounds in the +III and +V oxidation states. Bismuth (V) (bismuthate) exists only in solids (e.g. NaBiO₃, a powerful oxidant). In solution, only compounds of bismuth (III) are found. Bismuth (III) hydrolyses at pH 1-2, and shows no amphoteric properties. Bismuth (III) forms complexes with citrate, oxalate, iodide, thiosulphate and EDTA.

Spectrophotometric reagents for bismuth:

The conventional iodide and thiourea methods are simple and rapid, but lack sensitivity (1-5). Iodide method has been used to determine bismuth in a number of alloys (6-11). Dithizone forms an orange brown-dithizonate with bismuth, which is soluble in CHCl₃ and CCl₄ (12-15), and has been utilized to determine the metal in various materials (16-21). Other important reagents are: the dithiocarbamates, especially with sodium diethyl dithiocarbamate (22), pyrrolidinedithiocarbamate (23,24), pyrrosoledithiocarbamate (25), glycinedithiocarbamate (26), and dibenzyl dithiocarbamate (27,28), xylene orange (29-33), N-phenyl derivatives of thiourea + thiocyanate (34).
Other extractive spectrophotometric methods are based on the ion-pairs formed by bismuth halide complexes with thiolactams (35,36), dianipyrylmethylmethane (DAMM) and dianipyrylpropylmethane (DAPM)(37), 1,10-phenanthroline (38), chlorpromazine hydrochloride (39), tri-n-octylamine (40), benzylidemethylphenyl ammonium chloride (41), propyldithiopyrylmethane (42), ethylenediame-\( \text{\textit{N}} \cdot \text{\textit{N}'}-2,2'-\text{bis-(3-hydroxy propionic acid)}}(43), diacetyl bis-(isonicotinyl hydrazone) (44), 2-thiobarbituric acid (45) pyrogallol red (46), morpholine-4-dithioformate (47), alizarine red S (48), diethyldithiocarbamate (49), malachite green (50), dithiobi(antipyryl)methane (51), alizarine red in presence of basic dyes (52) and rhodamine B (53).

More sensitive methods for determining bismuth utilize the azo dyes; viz. thoron I (54), 1-(2-pyridylazo)-2-naphthol (PAN) (55,56), 4-(2-pyridylazo)resorcinol (57,58), 4-(2-pyridylazo)-1-naphthol (59), arsenazo III (60), pyrocatechol sulfonaphthalein complexon (61), semimethylenol blue (62), bismuthiol II (63), chlorophosphonazo III (64), halo-2-pyridylazo compounds (65), triphenylmethane dyes pyrocatechol violet (66), methylthymol blue (67), 5-(ethylamino)-2-(2-pyridylazo)-p-cresol and its bromo derivatives (68) and 1-(3,5-dibromo-pyridylazo)-cresol (69).

Further some new organic reagents recommended for the spectrophotometric determination of bismuth are bromopyrogallol red (70), 2,6-dimercapto-3,5-diphenylthiopyran-4-one
(71,72), 5-mercapto-3-((b-bromophenyl)-1,3,4-thiadiazole-2-
thonie (73), 1,3-bis [2-mercaptotheophyllinyl-(7')]-propane
(74), CMAB-oxime (75), quinoxaline-2,3-dithiol (76),
dithiopyrilmethane (77), 2-(5-bromo-2-pyridylazo)-5-diethyl-
aminophenol (78), 4,4'-bis-(2,3,5-trihydroxyphenylazo)-
diphenyl (79), 2-(3,5-dibromo-2-pyridylazo)-5-diethyl-
aminophenol and its haloderivatives (80), 2-(3,5-dibromo-
2-pyridylazo)-5-dimethylaminophenol (81), 7-methylanabasine-
-L-azo-p-cresol (82).

Present work:

Aqueous solution of THT formed dark red coloured
complex with bismuth (III) in weakly acidic medium. The
colour development was instantaneous and the complex was
stable. Detailed spectrophotometric studies were made
on this colour reaction to show the potentiality of this
reagent for the determination of bismuth.

EXPERIMENTAL

Bismuth (III) solution:

A stock solution of bismuth (III) was prepared by
dissolving an appropriate amount of bismuth nitrate
\[
\text{Bi(NO}_3\text{)}_3\cdot 5\text{H}_2\text{O}
\]
(AnalaR) in acidulated double
distilled water and was standardized using potassium iodide
spectrophotometrically (83).
Acetate buffer, pH 5.5:

An acetate buffer solution (83) was prepared by mixing 120 ml of 0.2N acetic acid and 880 ml of 0.2N sodium acetate solution in a 1 litre flask.

Dilute solution of sodium hydroxide and nitric acid were used for pH adjustment during preliminary investigations.

Spectral behaviour of the complex and effect of pH:

Absorption spectra of a series of solutions containing 1.0 ml of $2 \times 10^{-5}$M bismuth (III) and 1.0 ml of $1.0 \times 10^{-3}$M THT at different pH levels in a total volume of 25 ml were recorded against corresponding reagent blanks. It has been observed that only one complex of bismuth (III) is formed at all pH values absorbing maximum at $\lambda_{\text{max}} 530$ nm (fig. VI.1).

Plot of pH vs. absorbance at the $\lambda_{\text{max}} 530$ nm of the complexes showed that constant absorbance was exhibited in the pH range 4.0-6.5 (fig. VI.2). In subsequent studies, 2 ml of acetate buffer of pH 5.5 was used to maintain the appropriate pH.

Effect of reagent concentration:

To study the effect of reagent concentration on complex formation, a series of solutions containing 1.0 ml of $2 \times 10^{-5}$M of bismuth (III) and varying amounts of reagents was prepared followed by 2.0 ml of buffer solution in the final volume of
**Fig. VI.1. Absorption Spectra of Bi(III) - THT Complex at Different pH**

**Fig. VI.2. Effect of pH on Bi(III) - THT Complex**

Bi(III) = $8 \times 10^{-6}$ M

THT = $4 \times 10^{-5}$ M
25 ml. The absorbance was measured at 530 nm. It was observed that two times amount of THT with respect to the concentration of bismuth ion was required for complete complexation (fig. VI.3). In subsequent studies, at least five times molar excess of the reagent was maintained.

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

Linearity between the absorbance of the complex and bismuth (III) concentration was examined by varying the concentration of bismuth in the solution containing a fixed amount of ligand (sufficient excess) at pH 5.5 and measuring the absorbance at 530 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. VI.4), sensitivity, molar extinction coefficient and composition of the complex as determined by Job's method of continuous variations (fig.VI.5) are summarized in table VI.1.

Table VI.1: **Physico-chemical constants of bismuth (III)-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></td>
<td>530 nm</td>
</tr>
<tr>
<td>2.</td>
<td>Beer's law range</td>
</tr>
<tr>
<td></td>
<td>0.0 - 3.8 ppm</td>
</tr>
<tr>
<td>3.</td>
<td>Optimum concentration range</td>
</tr>
<tr>
<td></td>
<td>0.56 - 3.0 ppm</td>
</tr>
<tr>
<td>4.</td>
<td>Sandell's sensitivity</td>
</tr>
<tr>
<td></td>
<td>0.0038 ( (\mu g \text{ Bi(III)/cm}^2) )</td>
</tr>
<tr>
<td>5.</td>
<td>Molar extinction coefficient (( \epsilon ))</td>
</tr>
<tr>
<td></td>
<td>5.5 \times 10^4 ( (\text{l.mol}^{-1}\text{cm}^{-1}) )</td>
</tr>
<tr>
<td>6.</td>
<td>Molar composition by Job's method</td>
</tr>
<tr>
<td></td>
<td>2:3 (M:L)</td>
</tr>
</tbody>
</table>
**FIG. VI.3. EFFECT OF REAGENT CONCENTRATION ON Bi(III) - THT COMPLEX**

**FIG. VI.4. RINGBOM PLOT FOR Bi(III) - THT COMPLEX**
Fig. VI.5. Composition of Bi(III)-THT complex by Job's method.

Total molarity = $6 \times 10^{-5}$ M.
Recommended procedure:

To a suitable aliquot containing 14-75 μg of bismuth (III), add 2.0 ml of 1.0x10⁻³ M THT solution followed by 2.0 ml of acetate buffer solution. Make up the volume to 25 ml with distilled water. Measure the absorbance at 530 nm against a reagent blank prepared under similar conditions. Knowing the absorbance, bismuth content is deduced from the calibration curve.

Absorbance deviation and accuracy of the method:

The mean absorbance of a series of ten solutions containing 1 ml of 2x10⁻⁴ M of bismuth (III) and 2 ml of 1.0x10⁻³ M THT in total volume of 25 ml at pH 5.5 was found to be 0.44, with a standard deviation of 0.0016.

The accuracy of the method was checked by preparing a series of solutions containing different amounts of bismuth (III) in the range of 14-75 μg and 2 ml of 1.0x10⁻³ M THT and following the recommended procedure. The percentage error of the results of this series obtained was in the range 0.15 - 1.65% which showed the accuracy of the method was within the permissible limits accepted for spectrophotometric determinations.

Effect of diverse ions:

In the determination of bismuth (III) at the 1.7 μg/ml level, nitrate, nitrite, sulphite, sulphate, thiosulphate, phosphate, arsenate, citrate, tartrate, oxalate, thiourea,
thiosemicarbazide, alkaline earths, lanthanides, aluminium (III), chromium (III), and platinum metals did not interfere at all. However, sulphide, EDTA, zinc (II), manganese (II) and indium (III) were found to interfere. Results of tolerance limits, in parts per million of various ions in solution that caused a deviation smaller than $\pm 2\%$ in absorbance, are given in table VI.2.

**Table VI.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>Fluoride</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Chloride</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Bromide</td>
<td>150</td>
<td>-</td>
</tr>
<tr>
<td>Iodide</td>
<td>200</td>
<td>-</td>
</tr>
<tr>
<td>Cyanide</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>500</td>
<td>-</td>
</tr>
<tr>
<td>Cadmium (II)</td>
<td>10</td>
<td>masked by I⁻</td>
</tr>
<tr>
<td>Mercury (II)</td>
<td>12</td>
<td>masked by $S_2O_3^{2-}$</td>
</tr>
<tr>
<td>Iron (II)</td>
<td>20</td>
<td>masked by F⁻ or CN⁻</td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>10</td>
<td>masked by CN⁻</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>10</td>
<td>masked by CN⁻</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>25</td>
<td>masked by $S_2O_3^{2-}$</td>
</tr>
<tr>
<td>Lead (II)</td>
<td>20</td>
<td>masked by $S_2O_3^{2-}$</td>
</tr>
<tr>
<td>Silver (I)</td>
<td>20</td>
<td>masked by $S_2O_3^{2-}$ or T.U.</td>
</tr>
<tr>
<td>Antimony (III)</td>
<td>15</td>
<td>masked by CNS⁻</td>
</tr>
<tr>
<td>Thorium (IV)</td>
<td>25</td>
<td>masked by $PO_4^{3-}$</td>
</tr>
<tr>
<td>UC₂ (II)</td>
<td>5</td>
<td>masked by AsO₄^{3-}</td>
</tr>
</tbody>
</table>
Discussions

The principal photometric determination of bismuth (III) are as the iodide and as the complex with thio­urea (1-5). But it forms many binary complexes and some ternary ones of a reagent with the hexaiodobismuthate. Bismuth forms the orange yellow complex with an excess of iodide in acid medium (0.4 - 4N H₂SO₄)(1,2). Upto a concentration of 3% KI, the absorbance increases and above this concentration the absorbance remains constant. Preliminary separation of antimony is necessary. Besides antimony and bismuth, platinum (IV), palladium (II) and tin (IV) also form colored complexes and silver, thallium, copper and lead are precipitated. Halides viz. fluoride and chloride also weaken the colour. This method, however, has been applied for determining bismuth in steel (6), lead (5,7), chromium-nickel steel (8) and cast iron (9,11).

The dithizone (12-15) method is a highly sensitive and suitable for the determination of traces of bismuth (III) over the pH range 3-9.5, but the method is an extractive one. Lead, thallium (I) and tin (II) are also co-extracted with bismuth when cyanide and tartrate are used as masking agents; lead and thallium can be stripped into aqueous solution at pH ~ 3.3 and bismuth remains in the organic phase. If the amounts of zinc, cadmium and lead in the aqueous solution considerably exceed that of bismuth, then traces of these metals are also extracted. Higher concentrations of halides, citrate, acetate etc. also inhibit the extraction. This
method has been employed to determine bismuth in various samples viz., platinum samples (16), silver alloys (18), natural water (21), biological materials (12) etc.

Diethylidithiocarbamate (22) is a specific method for the spectrophotometric determination of bismuth. It forms coloured chelates with bismuth, which are soluble in organic solvent at 370 nm. But the complex is not very sensitive.

Cheng et al. (29-33) proposed a xylenol orange method for the determination of bismuth in acid medium. Zirconium, hafnium, tin (II) and antimony (III), which also form coloured complex with xylenol orange, they should be masked. Chloride, bromide and iodide decompose the bismuth-xylenol orange complex and should be absent.

Thiourea (1,2) is also a suitable spectrophotometric method. But the concentration of thiourea in the solution must be high. At higher concentration of some metals (Ag, Hg, Cu, Pb, Cd, Sn and Ti), precipitates are formed with thiourea. On the other hand, coloured complexes of antimony, palladium, lead, tin and titanium are also formed. The method is insensitive.

Among heterocyclic azo dyes, 1-(2-pyridylazo)-2-naphthol (55, 56) is a sensitive spectrophotometric reagent for bismuth. But the method is an extractive and details are lacking. Moreover, metal has been determined by exchange reaction. This method is based on the colour
reaction occurring when a solution containing copper-EDTA complex, alcoholic PAN and a suitable buffer is added to the solution of the sought-for metal. Bismuth, thus displaces an equivalent amount of copper (II) from the copper-EDTA complex and violet colour of the copper (II)-PAN complex appears.

4-(2-Pyridylazo)resorcinol forms red-coloured complex with bismuth (57,58) at pH 0-3.5 and the complex is extracted into tributylphosphate from 0.1-0.28 M nitric acid. But the sensitivity is very poor. Citrate, tartrate, sulphate and phosphate interfere.

In the present method THT forms a water-soluble complex with bismuth. More than sixty-fold excess of halides are tolerated. Cadmium (II), mercury (II), copper (II), lead (II), silver (I) have been masked by thiosulphate or iodide. 10-Fold excess antimony has been masked with thiocyanate. A few other metal ions viz. thorium, uranium, iron (II) etc. can also be masked. The method is fairly sensitive and can be compared with well known reagents known for the spectrophotometric determination of bismuth (table VI.3).

### Table VI.3: Sensitivities of the colour reactions of various reagents for bismuth

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Molar absorptivity (l. mol. (^{-1}) cm (^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea</td>
<td>3.6x10(^4)/322 nm</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>9.3x10(^3)/470 nm</td>
<td></td>
</tr>
<tr>
<td>Iodide</td>
<td>9.1x10(^3)/465 nm</td>
<td>4</td>
</tr>
<tr>
<td>Substance</td>
<td>Absorbance (µmol/L)</td>
<td>Wavelength (nm)</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>---------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Dithizone</td>
<td>7.92x10^4/490</td>
<td>12-15</td>
</tr>
<tr>
<td>Xylenol orange</td>
<td>2.4x10^4/540</td>
<td>30</td>
</tr>
<tr>
<td>Propylidithiopyrmethane</td>
<td>1.28x10^4/525</td>
<td>42</td>
</tr>
<tr>
<td>N-ethylendiamine-N,N'-2,2′-bis-(3-hydroxypropionic acid)</td>
<td>6.96x10^3/245</td>
<td>43</td>
</tr>
<tr>
<td>2-Thiobarbituric acid</td>
<td>2.4x10^4/416</td>
<td>45</td>
</tr>
<tr>
<td>Pyrogallol red</td>
<td>2.0x10^4/615</td>
<td>46</td>
</tr>
<tr>
<td>Morpholine-4-dithioformate</td>
<td>6.01x10^4/365</td>
<td>47</td>
</tr>
<tr>
<td>4-(2-Pyridylazo)resorcinal</td>
<td>1.07x10^4/515,530</td>
<td>58</td>
</tr>
<tr>
<td>2-(3,5-Dibromo-2-pyridylazo)-5-diethylaminophenol</td>
<td>5.9x10^4/595</td>
<td>81</td>
</tr>
<tr>
<td>2-(3,5-Dibromo-2-pyridylazo)-5-diethylaminophenol</td>
<td>3.0x10^4/600</td>
<td>80</td>
</tr>
<tr>
<td>N-methylanabasine-α-azo-p-creosol</td>
<td>7.63x10^3/550-60</td>
<td>82</td>
</tr>
<tr>
<td>Tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt.</td>
<td>5.5x10^4/530</td>
<td>Present method</td>
</tr>
</tbody>
</table>
Indium is similar to gallium and cadmium in its chemical properties. It occurs in aqueous solution exclusively in the +III oxidation state. The hydroxide, \( \text{In}(	ext{OH})_3 \), precipitates above pH 3-4 but, when freshly precipitated, redissolves in fairly concentrated alkali, thereby displaying weakly amphoteric properties. Yellow \( \text{In}_2\text{S}_3 \) precipitated at pH 2-3. Indium forms strong halide, oxalate, tartrate and EDTA complex.

**Spectrophotometric reagents for indium**

Important reagents for indium include as classes like hydroxy anthraquinones, triphenyl methane derivatives and azo dyes, as well as stilbazo and 3,4-dihydroxy azo benzene (1,2).

8-Hydroxyquinone (oxine)\(^{(84,85)}\) and 5,7-dibromo-8-hydroxyquinoline (bromo-oxine)\(^{(86-88)}\) react with indium ions in weak acid medium to form yellow, chloroform soluble chelates. Bromo-oxine or oxine was used for the spectrophotometric determination of indium in various materials \(^{(85-91)}\). Thiooxine (in toluene) has been used as extractive-spectrophotometric reagents for the metal \(^{(92)}\).

The most satisfactory reagents are methylthymol blue \(^{(93)}\), xylenol orange \(^{(94)}\), eriochrome cyanine R \(^{(95)}\), bromopyrogallol red \(^{(96)}\), catechol violet \(^{(97)}\), chrome azurol S \(^{(98)}\), 5,7-dichloro-8-hydroxyquinoline \(^{(99)}\),
dithizone (100), phenosafranine (101), phenylfluorone (102), rhodamine B (103), quercetin (104), chromotrope 2R(105), thiothenoyltrifluoroacetone (106) and pyrocatechol violet (107).

Indium (III) forms ternary complexes with the alizarine green dyes in the presence of cetyltrimethyl ammonium or cetylpyridinium ions (108).

Numerous azo dyes have been employed for the purpose to determine indium (III), a few of which are: 1-(2-pyridylazo)-2-naphthol (109,110), 4-(2-pyridylazo)resorcinol (PAR)(111), 4-(2-thiazolylazo)-resorcinol (TAR)(112), 1-(3,6-disulpho-2-thiazolylazo)-2-naphthol (113), 1-(4-carboxy-2-thiazolylazo)-2-naphthol (114), gallion (115), lumogallion (116), sulphonazo (117), sulphochlorophenol R (118), stilbazo (119), arsenazo I (120), thoron I (121), 3-(2-quinoxalylazo)dyhydroxopyridine (122), 2-(2-pyridylazo)-5-diethylamino)phenol (123), 4,4'-bis(3,4-dihydroxyphenylazo)-biphenyl (124), 6-(2-pyridylazo)-4-cyclohexylresorcinol (125), 4-(2-quinoxalylazo)resorcinol (126), 5-(2-pyridylazo)-2-monoethylamino-p-cresol (127), N-methylanabasine-α'-azo-p-cresol (128), 2-(3,4-dihydroxyphenylazo)thiazole (129) and N-methylanabasine-α'-azo-3,4-dimethylphenol (130).

**Present work:**

Indium (III) reacts with THT to form two water-soluble complexes, a dark red complex in acidic medium and a bluish-pink complex in alkaline medium. The colour reactions in both the medium have been investigated in detail for the spectrophotometric determination of indium as under.
EXPERIMENTAL

Indium (III) solution:

A stock solution of indium (III) was prepared by dissolving an appropriate amount of indium sulphate (AnalaR) in acidulated double distilled water and was standardized by 4-(2-pyridylazo)resorcinol (1).

Acetate buffer, pH 3.5:

An acetate buffer (83) solution was prepared by mixing 940 ml of 0.2N acetic acid and 60 ml of 0.2N sodium acetate solution in a 1 litre measuring flask.

Sodium carbonate solution:

0.04N sodium carbonate was prepared to maintain the alkaline pH.

Spectral behaviour of the complex and effect of pH:

Absorption spectra were recorded of a series of solutions containing 1.0 ml of 2.0x10^-4M indium (III) and excess of THT solution (1.0 ml of 1x10^-3M) at different pH levels in a total volume of 25 ml against corresponding reagent blanks. It has been observed that two complexes are formed at different pH levels, one a dark red coloured in acidic medium, absorbing maximum at 530 nm and another a bluish-pink coloured complex in alkaline medium absorbing maximum at 620 nm (fig. VI.6).
Plot of pH vs. absorbance for the red complex at 530 nm showed that constant absorbance was exhibited in the pH range 3.0 - 4.7 (fig. VI.7). Similarly 2 to 8 ml of 0.04N sodium carbonate solution was required to obtain the maximum and constant absorbance for the bluish pink complex (fig. VI.8). Subsequent studies on these complexes were carried out respectively at pH 3.5 with an acetate buffer (2.0 ml) and at pH ~10.5 maintaining it with 2 ml of 0.04N sodium carbonate solution.

**Effect of reagent concentration:**

The results for the effect of reagent concentration on complexation measured at 530 nm for the red and 620 nm for the blue complex showed that at least 3-and 4-times molar excess respectively of TBT were required for complete complexation (fig. VI.9). In subsequent studies, five-times molar excess of the reagent was used in each case.

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

The results obtained for the validity of Beer's law, optimum range of concentration for accurate determination as calculated from Ringbom plot (fig. VI.10), sensitivity, molar extinction coefficient and composition of complex as determined by Job's method of continuous variations (fig. VI.11) are summarised in Table VI.4.
FIG. VI. 6. ABSORPTION SPECTRA OF In(III) - THT COMPLEXES AT DIFFERENT pH

FIG. VI. 7. EFFECT OF pH ON In(III) - THT COMPLEX AT 530 nm
FIG. VI.8 - EFFECT OF SODIUM CARBONATE CONCENTRATION ON THE ABSORBANCE OF In(III) - THT COMPLEX AT 620 nm.

\[ \text{In(III)} = 8 \times 10^{-6} \text{ M} \]
\[ \text{THT} = 4 \times 10^{-5} \text{ M} \]

FIG. VII.9 - EFFECT OF REAGENT CONCENTRATION ON In(III) - THT COMPLEXES (A) pH 3.5, \( \lambda_{530} \) nm (B) in 8 x 10^{-3} N \( \text{Na}_2\text{CO}_3 \), \( \lambda_{620} \) nm.
FIG. VI.II. COMPOSITION OF In (III) - THT COMPLEXES BY JOB'S METHOD
(A) pH 3.5, λ 530 nm (B) IN 8 x 10^{-3} N Na_2 CO_3, λ 620 nm

FIG. VI.II. RINGBOM PLOT FOR In (III) - THT COMPLEXES AT
(A) pH 3.5, λ 530 nm (B) IN 8 x 10^{-3} N Na_2 CO_3, λ 620 nm

TOTAL MOLARITY
= 6 x 10^{-5} M

FIG. VI.II. COMPOSITION OF In (III) - THT COMPLEXES BY
JOB'S METHOD (A) pH 3.5, λ 530 nm (B) IN 8 x 10^{-3} N Na_2 CO_3, λ 620 nm
Table VI.4: Physico-chemical constants of the indium(III)-
THT complex

<table>
<thead>
<tr>
<th></th>
<th>Red complex</th>
<th>Bluish-pink complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\lambda_{\text{max}}$</td>
<td>530 nm</td>
<td>620 nm</td>
</tr>
<tr>
<td>2. Beer's law validity</td>
<td>0.0-1.8 ppm</td>
<td>0.0-1.3 ppm</td>
</tr>
<tr>
<td>3. Optimum concentration range</td>
<td>0.24-1.4 ppm</td>
<td>0.24-1.1 ppm</td>
</tr>
<tr>
<td>4. Sandell's sensitivity</td>
<td>0.0013 (μg In(III)/cm²)</td>
<td>0.0014 (μg In(III)/cm²)</td>
</tr>
<tr>
<td>5. Molar extinction coefficient ($\varepsilon$)</td>
<td>8.4x10⁴ (1. mol⁻¹cm⁻¹)</td>
<td>7.9x10⁴ (1. mol⁻¹cm⁻¹)</td>
</tr>
<tr>
<td>6. Molar composition by Job's method</td>
<td>1:2 (MIL)</td>
<td>1:3 (MIL)</td>
</tr>
</tbody>
</table>

Recommended procedure:

To a suitable aliquot containing 6-35 μg of indium (III) add 2.0 ml of 1x10⁻³M THT followed by 2.0 ml of acetate buffer solution or to an aliquot containing 6-27.5 μg of indium (III) add 2.0 ml of 1x10⁻³M THT followed by 2.0 ml of 0.04N sodium carbonate solution and make up the volume to 25 ml with distilled water. Measure the absorbance at 530 nm or 620 nm against a reagent blank prepared under similar conditions. Knowing the absorbance, indium content is deduced from the calibration curve.

Absorbance deviation and accuracy of the method:

The mean absorbance of a series of ten solutions containing 1 ml of 2x10⁻⁴M of indium (III) and 2.0 ml
of $1 \times 10^{-3}$ H$_2$THT in total volume of 25 ml was 0.672 with a standard deviation of 0.0024 at pH 3.5, and 0.632 with a standard deviation of 0.0015 at pH 10.5.

The accuracy of each method was checked by following the recommended procedure for indium (III) in a series of ten solutions containing different amounts of indium (III) in the range of 6-35 $\mu$g at pH 3.5 or 6-27.5 $\mu$g at pH $\sim$ 10.5. The percentage errors of the results of the series were 0.18 - 1.0% at pH 3.5 and 0.2 - 1.4% at pH 10.5.

**Effect of diverse ions:**

In the determination of indium (III) at the 0.36 $\mu$g/ml level, fluoride, chloride, bromide, iodide, nitrite, nitrate, sulphate, sulphite, thiosulphate, borate, phosphate, arsenate, thiourea, thiosemicarbazide, cyanide, thiocyanate, alkaline earths, lanthanides, aluminium (III), and chromium (III) all platinum metals did not interfere at all. However, sulphide, EDTA, manganese (II) and bismuth (III) interfered at pH 3.5, while only sulphide and EDTA were found to interfere at high pH ($\sim$ 10.5). Results of tolerance limits, in parts per million of various ions in solution that caused a deviation smaller than $\pm$ 2% in absorbance, are given in table VI.5.
Table VI.5: Effect of diverse ions

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Red complex (pH 3.5)</th>
<th>Bluish-pink complex (pH ~ 10.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount tolerated (ppm)</td>
<td>Masking if, any</td>
</tr>
<tr>
<td>Citrate</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td>Oxalate</td>
<td>160</td>
<td>-</td>
</tr>
<tr>
<td>Tartrate</td>
<td>220</td>
<td>-</td>
</tr>
<tr>
<td>Zinc(II)</td>
<td>4 masked by CN⁻</td>
<td>20 masked by CN⁻</td>
</tr>
<tr>
<td>Cadmium(II)</td>
<td>25 masked by CN⁻ or I⁻</td>
<td>28 masked by CN⁻</td>
</tr>
<tr>
<td>Mercury(II)</td>
<td>15 masked by S₂O₃²⁻ or I⁻</td>
<td>25 masked by S₂O₃²⁻ or I⁻</td>
</tr>
<tr>
<td>Manganese(II)</td>
<td>Interfered</td>
<td>10</td>
</tr>
<tr>
<td>Iron (II)</td>
<td>20 masked by F⁻ or CN⁻</td>
<td>40</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>20 masked by CN⁻</td>
<td>40</td>
</tr>
<tr>
<td>Cobalt(II)</td>
<td>20 masked by CN⁻</td>
<td>28</td>
</tr>
<tr>
<td>Copper(II)</td>
<td>40 masked by S₂O₃²⁻</td>
<td>64</td>
</tr>
<tr>
<td>Silver(I)</td>
<td>25 masked by S₂O₃²⁻</td>
<td>53</td>
</tr>
<tr>
<td>Lead(II)</td>
<td>20 masked by S₂O₃²⁻</td>
<td>15 masked by S₂O₃²⁻</td>
</tr>
<tr>
<td>Bismuth(III)</td>
<td>Interfered</td>
<td>7</td>
</tr>
<tr>
<td>Antimony(III)</td>
<td>10 masked by CNS⁻</td>
<td>10</td>
</tr>
<tr>
<td>Thorium(IV)</td>
<td>15 masked by PO₄³⁻</td>
<td>20</td>
</tr>
<tr>
<td>UO₂(II)</td>
<td>8 masked by AsO₄³⁻</td>
<td>24</td>
</tr>
</tbody>
</table>

Discussion:

Methods for determining indium are rather unselective, the separation methods are very important. The extractive
spectrophotometric method involving bromophenol blue and 8-hydroxyquinoline (oxine) react with indium ions in weak acid medium (pH 3.5 - 4.0) to form yellow, chloroform-soluble chelates. The absorption maximum of an indium bromo-oxinate solution in chloroform is at 415 nm, while the corresponding value for indium oxinate is at 395 nm. But these methods have poor selectivity.

Methyl thymol blue forms 1:1 and 1:2 complexes with indium in acidic medium at 600 nm; the latter complex is more appropriate for photometric determination. But aluminium, bismuth, nickel, ferric ion, EDTA, nitrilotriacetic acid, phosphate, citrate and oxalate interfere.

Bromopyrogallol red gives a 1:1 complex with indium at 570 nm in acidic medium. Colour developed is stable for 12 hrs. Separation of indium from possible interference by extraction as the bromide with butyl acetate is possible. But the sensitivity of the method is poor.

Catechol violet is another sensitive reagent but stannic, aluminium, bismuth, ferric, cupric and lead ions interfere. The complex is stable in the presence of gelatine.

The complex of rhodamine B with indium is appropriate for photometric reading for up to 0.025 mg of
indium per ml. For extraction from 1.5N sulphuric acid
-2M potassium bromide, appropriate solvents are 6:3:1 benzene
-isopropyl ether-acetlyacetone and 5:3:2 benzene:isopropyl
ether-methylisobutyl ketone. The extractive method is
tedious.

Quercetin (104) can replace morin as a spectro-
photometric reagent of similar structure for indium (III)
because of its greater availability. But aluminium,
fluoride, oxalate, and tartrate interfere.

The other suitable spectrophotometric reagent
for determination of indium is xylenol orange (94) and
absorbs at 560 nm (at pH 3.5). Beer's law is followed for
0.2 - 3 \text{ \mu g/ml}. But there is interference by bismuth,
stannous ion, tetravalent zirconium, hexavalent uranium,
pyrophosphate, dichromate, oxalate and EDTA.

Dithizone method (100) is applied for the determina-
tion of indium, after appropriate separation of the
metal from interferences. Lead, arsenic, antimony, tin,
thallium and cadmium interfere seriously. Higher concen-
tration of zinc also decreases the extraction.

4-(2-Pyridylazo)-resorcinol (PAR)(111) reacts
with indium to form two 1:1 and 1:2 water soluble
complexes at pH \sim 3 and pH \sim 6, respectively. Both
complexes are present at intermediate pH values, but
within the pH range from 6 to 8, only the 1:2 complex exist.
The method for determining indium at pH 6 is sensitive but not selective. At pH 3, the selectivity of the method increases, but the sensitivity decreases (132,133). Fe (II and III), Co, Mn, V, Zr, Bi, fluoride, oxalate and EDTA caused strong interference. Tin (II) and other strong reductants decolorise the reagent irreversibly.

1-(2-Pyrindylazo)-2-naphthol (PAN) (109, 110) is also suitable spectrophotometric reagent for indium. This reagent is equally as unselective as PAN and is somewhat less sensitive.

The present method is a highly sensitive method and selectivity has been increased by making use of cyanide, fluoride, iodide, thiosulphate etc. as masking agents. When the method is adopted at pH 3.5 only manganese (II), bismuth (III) interfered, while at pH $\approx 10.5$, only a few metals formed complexes and they all can be masked, thus making the method very selective at this pH. Comparison of sensitivities of some known methods also reveals the high sensitivities of the present methods (table VI.6).
Table VI.6: **Sensitivities of the Colour Reactions of Various Reagents for Indium**

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Molar absorptivity at $\lambda_{max}$ (l.mol$^{-1}$.cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-Hydroxyquinoline</td>
<td>$6.7 \times 10^3 / 395 \text{ nm}$</td>
<td>84, 85</td>
</tr>
<tr>
<td>Bromopyrine</td>
<td>$8.8 \times 10^3 / 415 \text{ nm}$</td>
<td>86-88</td>
</tr>
<tr>
<td></td>
<td>$6.7 \times 10^3 / 395 \text{ nm}$</td>
<td></td>
</tr>
<tr>
<td>Pyrocatechol violet</td>
<td>$1.9 \times 10^4 / 560 \text{ nm}$</td>
<td>107</td>
</tr>
<tr>
<td>Gallion</td>
<td>$2.2 \times 10^4 / 610 \text{ nm}$</td>
<td>115</td>
</tr>
<tr>
<td>Thoron I</td>
<td>$6.1 \times 10^3 / 520 \text{ nm}$</td>
<td>121</td>
</tr>
<tr>
<td>1-(2-Pyridylazo)-2-naphthol (PAN)</td>
<td>$1.9 \times 10^4 / 560 \text{ nm}$</td>
<td>110</td>
</tr>
<tr>
<td>$4$-(2-Quinolylazo)-resorcinol</td>
<td>$5.95 \times 10^4$</td>
<td>126</td>
</tr>
<tr>
<td>5-(2-Pyridylazo)-2-monooethylamino-p-cresol</td>
<td>$3.1 \times 10^4 / 535 \text{ nm}$</td>
<td>127</td>
</tr>
<tr>
<td>N-Methylanabasine-$\alpha$-azo-p-cresol</td>
<td>$1.28 \times 10^4 / 565 \text{ nm}$</td>
<td>128</td>
</tr>
<tr>
<td>Tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, tri sodium salt (THT)</td>
<td>$8.4 \times 10^4 / 530 \text{ nm}$</td>
<td>Present method</td>
</tr>
<tr>
<td></td>
<td>$7.9 \times 10^4 / 620 \text{ nm}$</td>
<td></td>
</tr>
</tbody>
</table>
Antimony occurs mainly in two oxidation states +III (antimonious compounds) and +V (antimonic compounds). The +III oxidation state is the most stable and hydrolyses at pH values as low as \( \sim 1 \), but the hydroxide \( \text{Sb(OH)}_3 \) dissolves at pH \( \sim 10 \) to form antimonite ion, \( \text{SbO}_2^- \). Antimony (V) is more acidic than antimony (III). Antimony (III) and (V) form sulphide, halide, tartrate and oxalate complexes as well as weak sulphate complexes.

**Spectrophotometric reagents for antimony:**

The extractive-spectrophotometric method for determining antimony based on the ion-association complexes of \( [\text{SbCl}_6]^- \) with rhodamine B and other basic dyes, are sensitive and selective. With rhodamine B (134-140), the antimony (V) chloride complex, forms a sparingly water-soluble ion-pair \( [\text{Rhod.}B]^+ [\text{SbCl}_6]^- \), which is extractable into benzene or di-isopropyl ether. Iodide is a classical method (141,142) and malachite green (143) and xanthene dyes (144) are used as extractive spectrophotometric reagents for antimony.

Other sensitive extractive-spectrophotometric methods based on ion-pair formation with \( \text{SbCl}_6^- \) are the triphenylmethane dyes (145), methyl violet (146-151), crystal violet (152-155) and brilliant green (156,157). Other basic dyes and reagents which have been used for the determination of the metal are methylene blue (158),
bromopyrogallol red (159), safranine 0 (160), antipyrine dyes (161, 162), pyrocatechol violet (163), 1,3,3-trimethyl-2-formylindolinium perchlorate (164), rhodamine S (165), dibromophenyl fluorone (166), morin (167), antipyryl bis [4-(benzylmethylamino)phenyl] methanol (168) and catechol violet (169). Mention of methylfluorone (170-173) and phenylfluorone (174, 175) can also be made as important methods for the determination of antimony.

Methods using coloured chelates of antimony (III) with azo dyes have been reported recently. These dyes include 4-(2-pyridylazo)resorcinol (PAR) (176), 1-(2-pyridylazo)-2-naphthol (177), 2-(5-bromo-2-pyridylazo)-5-(dimethylamino)-phenol (178), 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (179), 6-(2-pyridylazo)-3,4-dimethylphenol (180), 2-(3,5-dibromopyridylazo)-5-dimethylaminophenol (181), 6-(2-quinolylazo)-3,4-dimethylphenol (182), 2-(3,5-dibromo-2-pyridylazo)-5-diethylaminophenol (183), 3-(4-diethylaminophenylazo)-1,4-dimethyl-1,2,4-triazolium chloride (184), 5-ethylamino-2-(2-pyridylazo)p-cresol (185), 4-(6-methoxy-3-methylbenzothiazolin-2-ylazo)-N-methylidiphenylamine (186), N-methylanabasine-α-azo-6-m-aminophenol (187), N-methylanabasine-α-azodiethylaminophenol (188), 4-(2-N-methylanabasine-α-azo)-resorcinol (189), 4-(2-thiazoylazo)-catechol (190), 2-(2-quinolylazo)p-cresol (191) and 1-(2-quinolylazo)-2-naphthol (192).
Present work:

Antimony (III) forms a dark red coloured complex with THT in weakly acidic to neutral solutions. Investigations were made in detail on this colour reaction with a view to ascertain the potentiality of the reagent for spectrophotometric determination of antimony.

EXPERIMENTAL

Antimony (III) solution:

An appropriate amount of analytical grade antimony potassium (+)-tartrate (K$_3$SbO$_4$.H$_2$O$_6$) was dissolved in acidulated double distilled water and was standardized volumetrically (83).

Acetate buffer, pH 3.5:

An acetate buffer solution (83) was prepared by mixing 940 ml of 0.2N acetic acid and 60 ml of 0.2F sodium acetate solution to make up 1 litre.

Spectral behaviour of the complex and effect of pH:

A series of solutions containing 1.0 ml of $2\times10^{-4}M$ antimony (III) and excess of THT solution (1.0 ml of $1\times10^{-3}M$) was prepared and pH's were adjusted at different levels keeping total volume 25 ml. The spectra of the solutions were recorded against corresponding reagent blanks. All solutions of the series absorbed maximum at $\lambda$ max 535 nm (83:12)

A plot of pH vs. absorbance of the complex formed at $\lambda$ max (535 nm) showed that constant and maximum absorbance
was exhibited in the pH range 3.3-7.0 (fig. VI.13). The complexation reaction was studied at pH 3.5, the advantage at this pH being that a very few metals only formed complexes. For this purpose, 2.0 ml of acetate buffer of pH 3.5 was used in subsequent studies.

**Effect of reagent concentration:**

Study of the effect of reagent concentration on complexation showed that 4-times molar excess of TFT was sufficient for maximum complexation (fig. VI.14). However, in further studies at least 10-times molar excess of TFT 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. VI.15), sensitivity, molar extinction coefficient and composition as evaluated by Job's method of continuous variations (fig. VI.16) are summarized in table VI.7.

**Table VI.7 : Physico-chemical characteristics of the antimony (III) - TFT complex**

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \lambda_{\text{max}} )</td>
<td>535 nm</td>
</tr>
<tr>
<td>2</td>
<td>Beer's law range</td>
<td>0.0-4.5 ppm</td>
</tr>
<tr>
<td>3</td>
<td>Optimum concentration range</td>
<td>0.4-3.2 ppm</td>
</tr>
<tr>
<td>4</td>
<td>Sandell's sensitivity</td>
<td>0.0029 (( \mu \text{g Sb(III)/cm}^2 ))</td>
</tr>
<tr>
<td>5</td>
<td>Molar extinction coefficient (( \varepsilon ))</td>
<td>(4.16 \times 10^4 ) (1 mol.(^{-1}) cm (^{-1}))</td>
</tr>
<tr>
<td>6</td>
<td>Molar composition by Job's method</td>
<td>1:1 (M:M)</td>
</tr>
</tbody>
</table>
Fig. VI. 12. Absorption spectra of Sb(III) - THT complex at different pH.

Fig. VI. 13. Effect of pH on Sb(III) - THT complex.
FIG. VI.14. EFFECT OF REAGENT CONCENTRATION ON Sb(III)–THT COMPLEX

FIG. VI.15. RINGBOM PLOT FOR Sb(III)–THT COMPLEX

\[
\text{Sb (III)} = 8 \times 10^{-6} \text{ M}
\]
FIG. VI.16. COMPOSITION OF Sb(III)-THT COMPLEX BY JOB'S METHOD

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

$\text{ABSORBANCE}$

$\frac{[M]}{[M]+[R]}$
**Recommended procedure:**

To a suitable aliquot containing 10-80 μg of antimony (III), add 5.0 ml of 1.0x10⁻³M THT solution followed by 2.0 ml of acetate buffer solution and make up the volume to 25 ml. Measure the absorbance at 535 nm against a reagent blank prepared under similar conditions. Knowing the absorbance, antimony content 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 2x10⁻³M of antimony (III) and excess of THT in total volume of 25 ml at pH 3.5 was found to be 0.333, with standard deviation of 0.0025.

The accuracy of the method was checked by determining antimony in a series of ten solutions containing different amounts of metal between 10-80 μg, a fixed and excess amount of THT and following the recommended procedure. The percentage errors of the results of this series were in the range 0.24 - 1.7%, which showed the fair accuracy of the method, and lies in the permissible limits accepted for spectrophotometric determination.

**Effect of diverse ions:**

In the determination of antimony (III) at the 3.0 μg/ml level, fluoride, chloride, bromide, iodide, nitrite, nitrate, sulphite, sulphate, thiosulphate, citrate,
tartrate, oxalate, borate, phosphate, arsenate, thiourea, alkaline earths, lanthanides, aluminium (III), copper (II), molybdenum (VI), tungsten (VI) and platinum metals did not interfere at all. However, sulphide ions interfered seriously. Results of tolerance limits, in parts per million of various ions in solutions that caused a deviation smaller than ± 2% in absorbance, are tabulated in Table VI.C.

Table VI.C: Effect of diverse ions

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Amount tolerated (ppm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCN⁻</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>EDTA</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>Zinc (II)</td>
<td>20</td>
<td>masked by EDTA</td>
</tr>
<tr>
<td>Cadmium (II)</td>
<td>40</td>
<td>masked by EDTA</td>
</tr>
<tr>
<td>Mercury (II)</td>
<td>45</td>
<td>masked by EDTA</td>
</tr>
<tr>
<td>Iron (II)</td>
<td>50</td>
<td>masked by EDTA</td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>50</td>
<td>masked by EDTA</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>40</td>
<td>masked by EDTA</td>
</tr>
<tr>
<td>Silver (I)</td>
<td>8</td>
<td>masked by I⁻</td>
</tr>
<tr>
<td>Lead (II)</td>
<td>15</td>
<td>masked by ( S_{2}O_{3}^{2-} )</td>
</tr>
<tr>
<td>Indium (III)</td>
<td>10</td>
<td>masked by EDTA</td>
</tr>
<tr>
<td>Bismuth (III)</td>
<td>10</td>
<td>masked by EDTA</td>
</tr>
<tr>
<td>Thorium (IV)</td>
<td>25</td>
<td>masked by ( PO_{4}^{3-} )</td>
</tr>
<tr>
<td>( UO_{2}^{2+} )</td>
<td>10</td>
<td>masked by ( AsO_{4}^{3-} )</td>
</tr>
</tbody>
</table>
Discussion:

Most widely used methods for the determination of bismuth are based on ion-association complexes. Rhodamine B (134-140) is found to be more sensitive, but the disadvantage in this case is that metals forming chloride complexes which give the same reactions as antimony with Rhodamine B interfere in the determination. These metals are Au(III), Tl(III), Ga(III) and Fe(III), and thus make the method unsuitable.

The complex of trivalent antimony with iodide ion (141, 142) is read at various wavelengths. In 1:4 sulphuric acid, 425 nm is appropriate for reading against potassium iodide and in 1:10 sulphuric acid, the extinction at 330 nm is greater but more subject to interference, particularly bismuth interferes strongly.

Antipyrinyl [bis 4-(benzylmethylamino)phenyl] methanol (468) forms extractive complexes with antimony (V), which adheres to Beer's law for 0.04-1 μg of antimony per ml. There is interference by microgram amounts of thallous and auric ions and by mg amounts of ferric and stannic ion.

Brilliant green (156, 157) is also a suitable spectrophotometric reagent for the determination of antimony, which forms 1:1 orange coloured and extractive complex with antimony (V). But gold and thallium
interfere seriously. There is also some interference by chromate, bromide, thiocyanate, perchlorate, chlorate, and molybdate.

Catechol violet (169) forms 1:1 violet complex with antimony (V) in acidic medium. But molybdenum, lanthanum, manganese, tin, germanium, niobium, iron and gallium interfere.

Methylene blue (158) has been used in extractive photometric determination of antimony. But many metals interfere viz. gallium, thallic, auric, iodide or thiocyanate ions, and by more than 100-fold amounts of nitrate ion.

Morin (167) forms complexes with antimony and also with tin. The two elements are separated before determination. Extractions as iodides and re-extractions avoid interference. But the method seems to offer no particular advantage over other procedures.

Another reagent recommended for spectrophotometric determination of antimony is methylfluorone (170-173). In a weakly acidic medium the orange antimony (III) - methylfluorone complex, which exists as a stable sol in the presence of gelatin or poly (vinyl alcohol), is formed. But the method is less sensitive as well as less selective.
In recent years remarkable number of heterocyclic azo dyes were used for determination of antimony, but only a few were found for practical use. PAN (177) forms 1:1 complex at 585-595 nm. The complex can be extracted into chloroform. PAR (176) forms 1:2 complex with antimony (III) in 60% acetone at pH 1.2-1.9 Beer's law holds for 0.006-0.1 ug of antimony in 25 ml. The extraction of the complex with benzene both concentrates the materials and avoids many interferences.

A chloroform solution of 2-(2-quinolylazo)-p-cresol (191) extracts antimony (III). The extracted colour is stable for 8 hours. There are few interferences reported.

1-(2-Quinolylazo)-2-naphthol (192) is also a suitable azo reagents for the spectrophotometric determination of antimony. It forms 1:1 complex with antimony (III) in chloroform. But ferric and cupric ion interfere.

The present method is a highly selective method for the spectrophotometric determination of antimony (III) at pH 3.5, where only a few base metals interact with THT. More than 100-fold excess of EDTA does not interfere and has been used for masking most of those metals which show colour reaction with THT at pH 3.5. Sulphide decomposes the antimony (III) - THT complex quantitatively and advantage of this reaction has been taken to determine microamounts of sulphide ions indirectly. The sensitivity of the method is also high and a comparison can be made with well known methods for antimony (table VI.9).
Table VI.9: Sensitivities of the colour reactions of various reagents for antimony (III).

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Molar absorptivity at $\lambda_{\text{max}}$ (l. mol.$^{-1}$cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromopyrogallol red</td>
<td>$3.5 \times 10^4 / 560$ nm</td>
<td>159</td>
</tr>
<tr>
<td>Pyrocatechol violet</td>
<td>$3.32 \times 10^4 / 530$ nm</td>
<td>163</td>
</tr>
<tr>
<td>Xanthene dyes</td>
<td>$8.5 \times 10^4$ to $1.2 \times 10^5$</td>
<td>144</td>
</tr>
<tr>
<td>4,5-Dibromophenyl fluorone</td>
<td>$4.33 \times 10^4 / 540$ nm</td>
<td>166</td>
</tr>
<tr>
<td>Methylfluorone</td>
<td>$4.0 \times 10^4 / 530$ nm</td>
<td>170-173</td>
</tr>
<tr>
<td>1-(2-Pyridylazo)-2-naphthol</td>
<td>$1.56 \times 10^4 / 570$ nm</td>
<td>177</td>
</tr>
<tr>
<td>2-(5-Bromo-2-pyridylazo)-5-(dimethylamino)phenol</td>
<td>$4.8 \times 10^4 / 605$ nm</td>
<td>178</td>
</tr>
<tr>
<td>2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol</td>
<td>$5.5 \times 10^4 / 630$ nm</td>
<td>179</td>
</tr>
<tr>
<td>6-(2-Pyridylazo)-3,4-dimethylphenol</td>
<td>$8.5 \times 10^3 / 590$ nm</td>
<td>180</td>
</tr>
<tr>
<td>2-(3,5-Dibromopyridylazo)-5-dimethylaminophenol</td>
<td>$6.1 \times 10^4 / 620$ nm</td>
<td>181</td>
</tr>
<tr>
<td>Tri-(2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt (THT)</td>
<td>$4.16 \times 10^4 / 535$ nm</td>
<td>Present method</td>
</tr>
</tbody>
</table>

Present method
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