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Spectrophotometric Determination of Bismuth(III) and Indium(III) with 2,4,6-Tris(2-hydroxy-4-sulfo-1-naphthylazo)-1,3,5-triazine Trisodium Salt (THT)

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Reaction behavior of bismuth(III) and indium(III) with 2,4,6-tris(2-hydroxy-4-sulfo-1-naphthylazo)-1,3,5-triazine trisodium salt (THT) is established under various conditions. Bismuth(III) forms a 2 : 3 dark red complex (absorption maximum at 530 nm) with the reagent at pH 4—6.5. Indium(III) reacts with THT to form a 1 : 2 dark red complex at pH 3—4.7 (λ_{max} 530 nm) and a 1 : 3 purple blue complex at pH ca. 10.5 (λ_{max} 620 nm). The molar absorptivities for the color reactions are 5.5×10^4 for bismuth(III), 8.4×10^4 for indium(III) at pH 3.5 and 7.9×10^4 $L\cdot mol^{-1}\cdot cm^{-1}$ for indium(III) at pH ca. 10.5 (in sodium carbonate medium). Other physicochemical characteristics of the complexes are established. A number of foreign ions are tested for their interference and the use of masking agents wherever necessary is tabulated.

Recently, we proposed a water-soluble azo dye 2,4,6-tris(2-hydroxy-4-sulfo-1-naphthylazo)-1,3,5-triazine trisodium salt (THT) as chromogenic reagent for antimony and sulfide[1] and thorium and phosphate.[2] This reagent forms dark red color with bismuth(III) in weakly acidic medium and dark red and purple blue with indium(III) in weakly acidic and alkaline media, respectively. We propose spectrophotometric determination for these two elements in this communication.

Less attention has been given for microdetermination of bismuth and indium. Conventional iodide and thiourea methods[3,4] for bismuth are simple but lack sensitivity. Dithiocarbamate[5] is specific but is rather insensitive. Dithizone[3,4,6,7] has high sensitivity but the method is tedious and suffers lot of interferences. For indium, most of the methods are unselective and require separation of metals. Oxine[8,9] and bromo-substituted oxine[10—12] have been used as extractive reagents. However, PAR[13] is a better sensitive reagent for indium(III) at pH 6, but not selective. At pH 3, the selectivity increases, but sensitivity decreases.[14,15] The present reagent has been found to be highly sensitive, as well as selective for the determination of the two elements.

Experimental

Apparatus: A Bausch and Lomb Spectronic 2000 spectrophotometer with 10 mm matched glass cells was used for recording spectra and a Beckman Φ 60 pH meter was used for pH measurements.

Reagents: THT Solution: THT was synthesized as described earlier[1] and its 1×10^{-3} M solution (1M=1 mol dm^{-3}) was prepared by dissolving 0.900 g of THT in 1L of double-distilled water.

Bismuth(III) and Indium(III) Solution (1000 μg mL^{-1}): Standard solutions of bismuth(III) and indium(III) were prepared by dissolving an appropriate amount of bismuth nitrate pentahydrate $Bi(NO_3)_3\cdot5H_2O$ and indium sulfate monohydrate $In_2(SO_4)_3\cdot H_2O$ in double-distilled water and standardized by conventional methods.[16]

Acetate Buffer Solutions: Acetate buffer solution of pH 3.5 was prepared by diluting 940 mL 0.2 M acetic acid to 1L with 0.2 M sodium acetate and for pH 5.5, diluting 120 mL 0.2 M acetic acid to 1L with 0.2 M sodium acetate.

Sodium Carbonate Solution (0.02 M): Anhydrous sodium carbonate (2.12 g) was dissolved in 1L doubly distilled water for this concentration.

All the reagents used were of analytical grade during the experimental studies.

Procedures and Calibration Curves. Determination of Bismuth(III): To a suitable volume of sample containing 14—75 μg of bismuth(III) and 2 mL 1×10^{-3}M THT followed by 2 mL buffer solution of pH 5.5. Dilute to 25 mL with water and measure the absorbance at 530 nm against a corresponding reagent blank (2 mL 1×10^{-3}M THT+2 mL buffer diluted to 25 mL).

Determination of Indium(III): To a suitable volume of sample containing 6—35 μg of indium(III) add 2 mL 1×10^{-3}M THT followed by 2 mL of buffer solution of pH 3.5 or to an aliquot containing 6—27.5 μg of indium(III) and 2 mL 1×10^{-3}M THT followed by 2 mL 0.02 M carbonate solution. Make up the volume to 25 mL with water and measure the absorbance at 530 nm in the former case or at 620 nm for the latter against a corresponding reagent blank.

Deduce the amount of the metal ion from the standard calibration curve drawn under similar conditions.

Results and Discussion

Color Formation and Absorption Spectra. Bismuth(III) formed a dark red complex (absorption maximum at 530 nm) with an aqueous solution of THT at pH 4—6.5, while indium(III) formed two water soluble complexes, a dark red at pH 3—4.7 which absorbed maximally at 530 nm and a purple blue with a λ_{max} 620 nm. Color formation was instant and stable for several hours in each case. Acetate buffers were found siutable for maintaining weakly acidic pH's and thus 2 mL buffer of pH 5.5 for bismuth(III) and 2 mL buffer of pH 3.5 for indium(III) determinations were used. For determination of indium(III) at high pH, 2—8 mL 0.02 M sodium carbonate was found suitable and thus 2 mL of it was used in subsequent studies.

Table 1. Comparison of Sensitivities of Various Spectrophotometric Reagents for Bismuth(III) and Indium(III)

Reagent or reaction	Molar absorptivity (λ/nm) $L \cdot mol^{-1} \cdot cm^{-1}$ (for Bi)	Ref.	Molar absorptivity (λ/nm) $L \cdot mol^{-1} \cdot cm^{-1}$ (for In)	Ref.
Thiourea	3.6×10^4(322) 9.3×10^3(470)	3,4	—	
Iodide	9.1×10^3(645)	3,4	—	
Dithizone	7.92×10^4(490)	3,4	—	
Xylenol Orange	2.4×10^4(540)	17	—	
2,2′-(Ethylenediimino)bis[3-hydroxypropionic acid]	6.96×10^3(245)	18	—	
Propyldithiopyrylmethane	1.28×10^4(525)	19	—	
2-Thiobarbituric acid	2.4×10^4(416)	20	—	
Pyrogallol Red	2.0×10^4(615)	21	—	
Morpholine-4-dithioformate	4.01×10^4(615)	21	—	
8-Quinolinol (Oxine)	—		6.7×10^3(395)	8,9
5,7-Dibromo-8-quinolinol	—		8.8×10^3(415)	10
Pyrocatechol Violet	—		1.9×10^4(560)	27
Gallion	—		2.2×10^4(610)	28
Thoron I	—		6.1×10^3(520)	29
2-(3,5-Dibromo-2-pyridylazo)-5-dimethylaminophenol	9.9×10^4(600)	24	—	
2-(3,5-Dibromo-2-pyridylazo)-5-diethylaminophenol	8.0×10^4(600)	25	—	
N-Methylanabasine-α-azo-*p*-cresol	7.63×10^3 (550—600)	26	1.28×10^4(565)	30
4-(2-Pyridylazo)resorcinol (PAR)	1.07×10^4 (515, 530)	23	4.3×10^4(510) 1.8×10^4(510)	13—15
1-(2-Pyridylazo)-2-napthol (PAN)	—		1.9×10^4(560)	31
4-(2-Quinolylazo)resorcinol.	—		5.95×10^4	32
5-(2-Pyridylazo)-2-ethylamino-*p*-cresol	—		3.1×10^4(535)	33
2,4,6-Tris(2-hydroxy-4-sulfo-1-naphthylazo)-1,3,5-triazine trisodium salt (THT)	5.5×10^4(530)	Present method	8.4×10^4(530) 7.9×10^4(620)	Present method

The effect of THT concentration was investigated in each case at their respective λ_{max}'s containing a constant amount of bismuth(III) or indium(III) and varying amounts of the reagent. It was found that 2 times molar excess of THT was required for bismuth(III), while 3—4 times molar excess of THT was necessary for complete complexation for indium(III) at both pH levels. All further experiments were carried out with at least 5-fold molar excess of the reagent solution.

Other Characteristics of the Complexes. The complexes obeyed Beer's law over the range 0—3.8 ppm of bismuth(III) and 0—1.8 ppm at pH 3.5 and 0—1.3 ppm at pH ca. 10.5 of indium(III). The optimum concentration ranges as evaluated by Ringbom's plot are 0.56—3.0 ppm of bismuth(III) and 0.24—1.4 or 0.24—1.1 ppm of indium(III), at low and high pH, respectively. These are the optimum ranges in which the metal ions could be accurately determined. The respective Sandell's sensitivities of the bismuth(III) complex and indium(III) complexes at low and high pH are 0.0038, 0.0013, and 0.0014 $\mu g\, cm^{-2}$ with their respective molar absorptivities (ε), 5.5×10^4, 8.4×10^4, and 7.9×10^4 $L \cdot mol^{-1} \cdot cm^{-1}$. Table 1 gives a comparison of the sensitivities of some methods used for the determination of bismuth(III) and indium(III).

Table 2. Effect of Diverse Ions on the Determination of 1.7 $\mu g\, mL^{-1}$ of Bismuth(III)

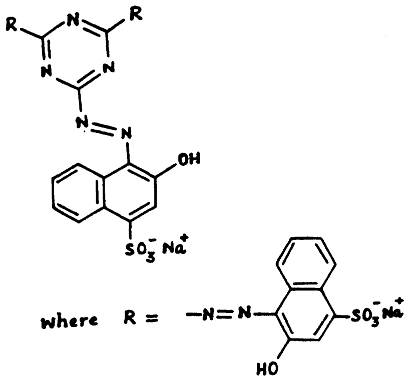
Foreign ions	Tolerance limits in ppm	Masking agent
Fluoride	100	—
Chloride	100	—
Bromide	150	—
Iodide	200	—
Cyanide	400	—
Thiocyanate	500	—
Cadmium(II)	10	Masked by I^-
Mercury(II)	12	Masked by $S_2O_3^{2-}$
Iron(II)	20	Masked by CN^-
Cobalt(II)	10	Masked by CN^-
Nickel(II)	10	Masked by CN^-
Copper(II)	25	Masked by $S_2O_3^{2-}$
Lead(II)	20	Masked by $S_2O_3^{2-}$
Silver(I)	20	Masked by $S_2O_3^{2-}$
Antimony(III)	15	Masked by CNS^-
Thorium(IV)	25	Masked by PO_4^{3-}

The stoichiometric ratios of metal to ligand in the complexes under the conditions mentioned above, were determined by Job's method of continuous variations. In case of indium(III) complexes, it was confirmed that the metal to ligand ratio was 1 : 2 for the dark red and 1 : 3 for the purple blue complexes. However, bismuth(III) unusually formed 2 : 3 com-

Table 3. Effect of Diverse Ions on the Determination of 0.86 μg mL^{-1} of Indium(III)

	Red complex (pH 3.5)		Purple-blue complex (pH ca. 10.5)	
Foreign ion	Tolerance limits in ppm	Masking agent	Tolerance limits in ppm	Masking agent
Citrate	250	—	180	—
Oxalate	160	—	150	—
Tartrate	220	—	150	—
Zinc(II)	4	Masked by CN$^-$	20	Masked by CN$^-$
Cadmium(II)	25	Masked by CN$^-$ or I$^-$	28	Masked by CN$^-$
Mercury(II)	15	Masked by $S_2O_3^{2-}$ or I$^-$	25	Masked by $S_2O_3^{2-}$ or I$^-$
Iron(II)	20	Masked by F$^-$ or CN$^-$	40	—
Manganese(II)	Interfere	—	10	—
Nickel(II)	20	Masked by CN$^-$	40	—
Cobalt(II)	20	Masked by CN$^-$	28	—
Copper(II)	40	Masked by $S_2O_3^{2-}$	64	—
Silver(I)	25	Masked by $S_2O_3^{2-}$	53	—
Lead(II)	20	Masked by $S_2O_3^{2-}$	15	Masked by $S_2O_3^{2-}$
Bismuth(III)	Interfere	—	7	—
Antimony(III)	10	Masked by CNS$^-$	10	—
Thorium(IV)	15	Masked by PO_4^{3-}	20	—
UO_2(VI)	Interfere	—	24	—

plex. THT(**1**) is a multidentate ligand$^{1)}$ and a tentative structure for bismuth(III)-THT complex could be given as **2**. The complexes are not extractable in organic solvents and thus show the ionic character.



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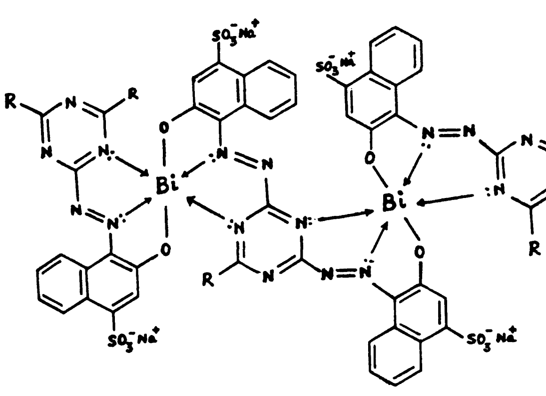

2

Effect of Diverse Ions on the Determination of Bismuth(III) and Indium(III). In the determination of bismuth(III) at the 1.7 μg mL^{-1} level, nitrite, nitrate, sulfite, sulfate, thiosulfate, phosphate, citrate, tartrate, oxalate, thiourea, thiosemicarbazide up to 1000-fold excess, alkaline earths, lanthanoids, aluminium(III), chromium(III), and platinum metals up to 50-fold excess did not interfere. However, sulfide, EDTA, zinc(II), manganese(II), uranyl(VI), and indium(III) were found to interfere.

In the determination of indium(III) at the 0.86 μg mL^{-1} level, fluoride, chloride, bromide, iodide, nitrite, nitrate, sulfite, thiosulfate, borate, phosphate, thiourea, thiosemicarbazide, cyanide, thiocyanate up to 1000-fold excess and alkaline earths, lanthanoids, aluminium(III), chromium(III), platinum metals up to 50-fold excess did not interfere. However, sulfide, EDTA, manganese(II), uranyl(VI), and bismuth(III) interfered at pH 3.5, while only sulfide and EDTA were found to interfere at high pH (ca. 10.5).

Tables 2 and 3 represent the tolerance limits in ppm of various ions in solution that caused a deviation smaller than ±2% in absorbance for the determination of bismuth(III) and indium(III) respectively.

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