

of ammonia (sp. gr. 0.88) to ammonium chloride (7 g) and diluted to 100 ml. All other reagents used were of the AR quality.

Optimum conditions for the determination of each metal, viz. Co(II), Ni(II) and Cu(II), using AHP-4S, DHP-4S, and CPD-4S as indicators, have been worked out and the results are presented in Table 1.

Procedure—To a suitable aliquot containing 0.3-7.1 mg of Co(II), 0.3-8.8 mg of Ni(II) or 0.32-25.4 mg of Cu(II) were added 2-3 drops of 0.25% of AHP-4S, DHP-4S or CPD-4S and 5 ml of $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$, $\text{KH}_2\text{PO}_4/\text{NaOH}$ or sodium acetate/acetic acid buffers (Table 1). The volume was made up to 20 ml by adding doubly distilled water. The contents were titrated against standard EDTA solution taken in microburette till the end point is reached (Table 1). The titrations can be performed in reverse manner also (by taking EDTA solution in the titration flask and titrating it against the metal ion solution from the burette) with equal ease and accuracy.

Statistical evaluation of results (Table 1) have been carried out by titrating six identical solutions.

Effect of diverse ions—To explore the possibility of performing titrations in the presence of various ions (anions and cations), titrations were performed by taking 2.359 mg of Co(II), 2.347 mg of Ni(II) and 2.543 mg of Cu(II), adding foreign ions in varying proportions and following the above procedure. Masking agents were also used to eliminate interference of some of the cations and anions.

In the case of Co(II) anions like F^- , Br^- , I^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, NO_3^- , NO_2^- , CNS^- , $\text{C}_2\text{O}_4^{2-}$, $\text{S}_2\text{O}_8^{2-}$, citrate, tartrate, WO_4^{2-} , MoO_4^{2-} , S^{2-} , thiourea, BO_3^{3-} and CH_3COO^- do not interfere when present up to 5000 ppm level. However, CN^- , Ni^{2+} , Cu^{2+} , Mn^{2+} and In^{3+} interfere. The following cations do not interfere (amounts in ppm) in the presence of masking agent mentioned in brackets: Pb^{2+} (2:1) (I^-), Zn^{2+} (1:3) (tartrate), Cd^{2+} (1:2) (I^-), Hg^{2+} (5000) (I^-), Sb^{3+} (609), UO_2^{2+} (5000), Sn^{2+} (100-1000) (F^-), Ru^{3+} (20), Ge^{4+} (1000) and Ag^+ (5000) (I^-).

For Ni(II) anions like F^- , Br^- , I^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, NO_3^- , ClO_4^- , BO_3^{3-} and CH_3COO^- , tartrate up to 5000 ppm level and CNS^- , $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$ and citrate up to 1000 ppm, do not interfere. However, S^{2-} , CN^- , Co^{2+} , Cu^{2+} and In^{3+} interfere. The interference due to most of the other cations could be eliminated by using masking agents.

In copper titration anions like F^- , Br^- , I^- , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, NO_3^- , NO_2^- , CNS^- , tartrate, PO_4^{3-} , ClO_4^- , BO_3^{3-} , $\text{S}_2\text{O}_8^{2-}$, SO_3^{2-} and citrate do not interfere up to 5000 ppm level. However, CN^- , Co^{2+} , Ni^{2+} , Mn^{2+} and In^{3+} interfere. The interference due to common cations could be obviated using common masking agents.

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2-Mercapto-4,4,6-trimethyl-1H,4H-pyrimidine as a Spectrophotometric Reagent for Bi(III) & Te(IV)

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2-Mercapto-4,4,6-trimethyl-1H,4H-pyrimidine reacts with Bi(III) to give an orange-red precipitate which is quantitatively extracted by chloroform from 1.5-3.0N perchloric acid. The complex in chloroform exhibits maximum absorbance at 500 nm (ϵ -12700) and the colour is stable for 48 hr. Under similar conditions the reagent gives a yellow coloured solution with Te(IV) showing maximum absorbance at 385 nm (ϵ -12600). The Beer's law is obeyed up to 17.0 ppm and 7.0 ppm for Bi(III) and Te(IV) respectively. Based on these reactions simple spectrophotometric methods for Bi(III) and Te(IV) alone or in the presence of various foreign ions have been developed.

NUMEROUS reagents have been investigated from time to time for spectrophotometric determination of bismuth^{1,2}. However, for tellurium only few suitable chromogenic reagents³ are known. In the course of studies on biologically important substituted pyrimidines as analytical reagents³⁻⁵ it was found that 2-mercapto-4,4,6-trimethyl-1H,4H-pyrimidine (MTPm) reacted with Bi(III) in highly acidic medium to give an orange-red precipitate extractable in chloroform. While under similar conditions this reagent formed a yellow coloured solution with Te(IV); this has been made the basis of spectrophotometric methods for the determination of Bi(III) and Te(IV). Other derivatives of pyrimidine such as N-ethyl-2-mercapto-4,4,6-trimethyl-1H,4H-pyrimidine, N-n-butyl-2-mercapto-4,4,6-trimethyl-1H,4H-pyrimidine, N-phenyl-2-mercapto-4,4,6-trimethyl-1H,4H-pyrimidine, N-anisyl-2-mercapto-4,4,6-trimethyl-1H,4H-pyrimidine and N-p-nitrophenyl-2-mercapto-4,4,6-trimethyl-1H,4H-pyrimidine were also tried without success.

Though the orange-red precipitate can also be extracted by CCl_4 or benzene but the best results are obtained with chloroform. The coloured complex of bismuth shows maximum absorbance at 500 nm (ϵ -12700) and is stable for 48 hr. Sandell's sensitivity of the reaction was calculated to 0.0166 $\mu\text{g Bi/cm}^2$ for 0.001 absorbance. The absorbance remained maximum and constant in the presence of 1.5-3N perchloric acid. In this acid region the extraction of the coloured complex by chloroform is quantitative, i.e. 100%. Sulphuric acid and nitric acid were also found equally good, but serious interference was observed with hydrochloric acid. For full colour development, 80-fold molar excess of MTPm over bismuth was needed.

Te(IV) reacted with MTPm in the acid range 1.3-2.5N HClO_4 to give a stable yellow coloured solution as a result of complex formation (λ_{max} 385;

TABLE 1 — EFFECT OF FOREIGN IONS

(Absorbance in the absence of foreign ions for bismuth complex = 0.635; absorbance in the absence of foreign ions for tellurium complex = 0.630)

Foreign ion	Amount of foreign ion tolerated with Bi (10.5 ppm)	Deviation in absorbance	Amount of foreign ion tolerated with Te (6.4 ppm)	Deviation in absorbance
F ⁻	500	-0.005	500	-0.005
Cl ⁻ or Br ⁻	20	-0.008	100	-0.005
CN ⁻	50	-0.002	25	-0.004
NO ₃ ⁻	2000	-0.005	1000	-0.002
SCN ⁻	100	-0.010	50	-0.008
CH ₃ COO ⁻	3000	-0.002	3000	-0.002
SO ₃ ²⁻	2000	-0.005	2000	-0.002
S ₂ O ₃ ²⁻	100	-0.007	40	-0.005
C ₂ O ₄ ²⁻	2000	-0.002	1000	-0.001
EDTA	400	-0.005	400	-0.008
BO ₃ ³⁻	3000	-0.001	2000	-0.002
PO ₄ ³⁻	2000	-0.004	1000	-0.005
Citrate or tartrate	3000	-0.001	1000	-0.005
Ca ²⁺ or Sr ²⁺ or Ba ²⁺	1000	+0.002	1000	+0.002
Zn ²⁺ or Cd ²⁺	200	+0.005	100	+0.008
Sn ²⁺	200	+0.002	100	+0.002
Pb ²⁺	20	+0.008	20	+0.005
Co ²⁺	80	+0.002	40	+0.008
Ni ²⁺	80	+0.002	40	+0.006
Au ³⁺	10	+0.008	10	+0.010
As ³⁺	50	+0.001	50	+0.005
Ru ³⁺ or Rh ³⁺ or Ir ⁴⁺	10	+0.005	5	+0.010
Ti ⁴⁺ or Zr ⁴⁺	50	+0.002	50	+0.002
Pt ⁴⁺	25	+0.001	10	+0.010

€ 12600). The complex is not extractable in organic solvents. Sandell's sensitivity was found to be 0.0101 µg Te/cm² for 0.001 absorbance. Nearly 70-fold molar excess was needed for full colour development.

Beer's law is obeyed up to 17.0 ppm (500 nm) and 7.0 ppm (385 nm) for Bi(III) and Te(IV) respectively. The optimum ranges for accurate determination as deduced from Ringbom plots were 4.0-14.6 ppm and 1.5-7.0 ppm for Bi(III) and Te(IV) respectively.

The stoichiometry of Bi(III) and Te(IV) complexes as determined by logarithmic and Asmus methods (Job's method was not found suitable) was found to be 1:3 and 1:2 (metal: ligand) respectively.

Stock solutions of Bi(III) and Te(IV) were prepared by dissolving appropriate amounts of spectroscopically pure bismuth metal (Johnson Matthey, UK, specpure) and tellurium dioxide (BDH, AR) in 1.0N perchloric acid and they were standardized. All other solutions were prepared from AR grade chemicals and deionized water. 2-Mercapto-4,4,6-trimethyl-1H,4H-pyrimidine was prepared by the method of Mathes⁶ and its solution was prepared by dissolving requisite amount in 0.2N perchloric acid.

Determination of Bi(III) — To an aliquot containing bismuth in the concentration range 40-146 µg, were added 2-3 ml of 8N HClO₄ and 6 ml of 0.01M pyrimidine solution (in 0.2M HClO₄). The mixture was diluted to 10 ml, shaken and extracted with chloroform (10 ml) for 20 min. The organic layer was separated and its absorbance measured at 500 nm against a chloroform blank. The metal concentration was calculated by comparing with a precalibrated graph.

Determination of Te(IV) — To Te(IV) solution (concentration between 15.0 and 70.0 µg) were added 6 ml of 0.01M of MTPm, followed by 2-3 ml of 8N HClO₄. The mixture was diluted to 10 ml and its absorbance was measured at 385 nm against a reagent blank. The amount of tellurium was calculated from a standard curve.

Effect of diverse ions — Tolerance limits of various foreign ions were calculated in the determination of 10.5 ppm of bismuth and 6.4 ppm of tellurium and the results are presented in Table 1. However I⁻, NO₂⁻, thiourea, Cu²⁺, Ag⁺, Hg²⁺, Sb³⁺, V⁴⁺, Se⁴⁺ and Os⁸⁺ even at 1.0-2.0 ppm level, affect the determination seriously. In the determination of Bi(III), 10.0 ppm of each copper (with EDTA) and palladium with (S₂O₃²⁻) can be masked. Ag⁺, Hg²⁺ and Os⁸⁺ can also be tolerated up to 5.0 ppm level using CN⁻ as masking agent.

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