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QUANTITATIVE ESTIMATIONS OF ANTIMONY(III), MERCURY(II) AND BISMUTH(III) WITH 1,3-DIMORPHOLINOPROPANE

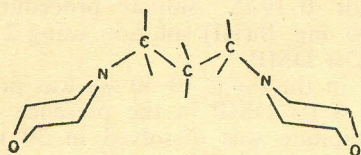
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Abstract. New quantitative procedures for the determination of Sb(III), Hg(II) and Bi(III) based on their precipitation with 1,3-dimorpholinopropane are reported. The precipitates are obtained in acidic solutions in the presence of an excess of iodide. The compound are weighed as $[C_{11}H_{22}O_2N_2H_2][SbI_4]_2$, $[C_{11}H_{22}O_2N_2H_2][HgI_4]$ and $[C_{11}H_{22}O_2N_2H_2][BiI_5]$ and have the lowest chemical factors so far reported. In case of Bi(III) quantities less than 50 mg, the precipitate was dissolved in dimethylsulphoxide and subjected to spectrophotometric measurement at suitable wavelengths.

The coordination chemistry,¹⁻³ and the industrial⁴⁻⁶ and analytical uses⁷⁻¹⁰ of N,N'-dimorpholinoethane (DME), a ligand derived from ethylenediamine have been studied in the past. However, various N,N'-alkyldiaminopropanes and system derived from 1,3-diaminopropane received relatively less attention. The coordination chemistry of the ligand N,N'-dimorpholinopropane(I)(DMP) has only recently been reported¹¹⁻¹² and its uses as a selective analytical reagent have so far remained unexplored. DMP



(I)

provides a more favourable i.e. wider bite angle than DME leading to increased stability of the metal complexes¹³ It also has a better gravimetric factor than DME (and other reagents) and should, therefore, be a better reagent for estimation of various metal ions and anions.

DMP forms sparingly soluble, thermally stable, crystalline compounds with Sb(III), Hg(II) and Bi(III) in acid solutions and in the presence of excess of iodide. These compounds permit an excellent gravimetric and spectrophotometric determination of the said metal ions. New procedures for such determinations using DMP as a precipitating reagent are described here.

Experimental

Materials. Metals and their salts were obtained from sources specified at appropriate places and were used without further purification. Solvents were normally distilled before use. The ligand DMP was prepared according to the procedure of Gero.¹⁴

Physical Measurements. The elemental analysis

was performed by Dr. F.B. Strauss of Microanalytical Laboratory, Oxford (England). Metal ions were estimated using usual analytical procedures.¹⁵ The spectrophotometric measurements were done on Beckman D.U. spectrophotometer using 1-cm quartz cell. The pH of the solutions were measured with Radelkis (Hungary) pH meter using appropriate electrodes. The m.p.s. were determined on Electrothermal (England) m.p. apparatus and are reported uncorrected. All weighings were done on a five-place electrical Mettler balance.

Preparation of the Standard Metal Ions Solution

(a) Standard Sb(III) solution was prepared by dissolving 228.1 mg SbCl₃ (10 mm) Polskil Chemiczne, Poland) in known volume of 2N HCl.

(b) Standard Hg(II) solution was prepared by heating 2.7g (9.95 mm) HgCl₂ (Chemapol, Czechoslovakia) in 100 ml water to obtain a clear solution which was diluted to one liter so that 100 ml of the resulting solution corresponds to 197.7 mg of Hg(II).

(c) Standard Bi(III) solution were prepared by dissolving 2 g (9.57 mm) Bi metal (Griffin and Tatlock) in 50 ml conc HCl containing 3 ml conc HNO₃ and diluting it to 1 litre. The pH of the resulting solution was found to be 0.4.

Estimation of Sb(III). KI (4.2 g) dissolved in 1N HCl was added to solutions containing 25-250 mg Sb(III) in 2N HCl. The solution was further diluted by 30 ml water and 2-3 ml SO₂ water was added. A yellow precipitate was formed on adding 6 ml 0.25M DMP in HCl. The precipitate was filtered through a sintered glass crucible, washed thrice with 5 ml washing solution containing 35 ml 1N HCl + 17 ml 57% HI + 6.3 ml SO₂ water + 2 ml 0.25M DMP solution and finally twice with 2 ml ether. The precipitate was dried at 140° for 1-3 hr and weighed as $[C_{11}H_{22}O_2N_2H_2][SbI_4]_2$, factor, 0.1651.

Estimation of Hg(II). To a practically neutral solution of HgCl₂ containing 25-250 mg Hg(II) was added 0.5 g KI and 20-30 ml 0.5M HCl. The solution was diluted to 300 ml and 20-30 ml 0.1M DMP

TABLE 1. ANALYTICAL DATA OF DMP COMPOUNDS.

Compound	Colour	Dec. pt (°C)	Metal (%)		C(%)		H(%)		N(%)	
			Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
C ₁₁ H ₂₂ O ₂ N ₂ 2SbI ₃ 2HI	Yellow	255	16.40	16.51	8.89	8.96	1.62	1.64	1.93	1.90
C ₁₁ H ₂₂ O ₂ N ₂ HgI ₂ 2HI	White	185	21.63	21.70	14.21	14.29	2.59	2.62	3.14	3.03
C ₁₁ H ₂₂ O ₂ N ₂ BiI ₃ 2HI	Orange	220	20.46	19.72	12.44	12.47	2.28	2.28	2.41	2.64

TABLE 2. ESTIMATION OF Sb(III) USING DMP AS GRAVIMETRIC REAGENT.

Wt of Sb(III) taken (mg)	Found		Absolute deviation
	Wt of ppt (mg)	Calcd Sb(III) (mg)	
41.2	251.4	41.5	+ 0.3
92.9	566.9	93.6	+ 0.7
113.4	697.8	115.2	+ 1.8
150.8	921.4	152.1	+ 1.3
170.8	1029.2	169.9	- 0.9
190.7	1152.1	190.2	- 0.5
200.2	1219.4	201.3	+ 1.1

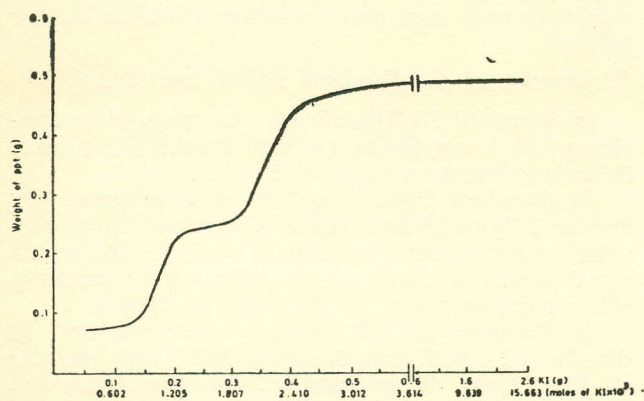
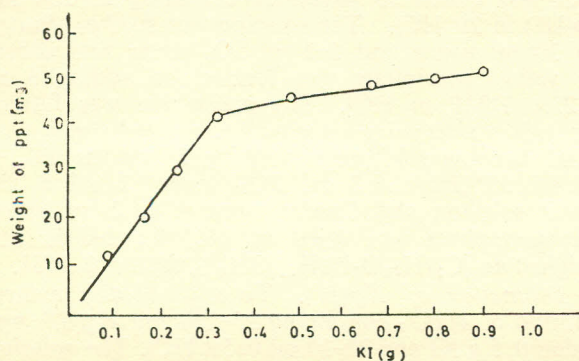


Fig. 1. Weight of the precipitate obtained from 50 mg of Bi (III) as a function of iodide concentration.

Fig. 2. Weight of DMP, 2SbI₃.2HI precipitate obtained from 121.8 mg Sb(III) as a function of iodide concentration.

solution was added dropwise with constant stirring. White needle-like crystalline precipitate was formed almost immediately and the pH of the solution was found to be 3.0. The solution was allowed to stand for about an hour. The solid was filtered out in a sintered glass crucible, washed with 2-3 ml ether and weighed as Hg(DMP)I₂.2HI after drying for about 1 hr at 110°, factor 0.21696.

Estimation of Bi(III) in Quantities more than 50 mg. Five gram (30.1 mM) KI in 20 ml of water was slowly added to 100 ml of the solutions containing 100-200 mg of Bi (III). The solution was further diluted by 40 ml water and 12 ml 0.5M DMP solution was added dropwise with constant stirring. The pH of the solution changed from 0.4 to 0.9, orange coloured crystalline precipitate was immediately formed. The solution was allowed to stand for about 2 hr at room temperature and the precipitate was filtered through a sintered glass crucible (Pyrex Por 4), washed three times with 2 ml water, dried for 2 hr at 110-115° and weighed as Bi(DMP)I₃.2HI, factor 0.1972. Similar procedure was used for 50-100 mg Bi(III) solution using 2.5 g KI and 12 ml 0.25M DMP.

Bi(III) in the range 10-50 mg was precipitated by 10 ml of 0.1M DMP in the presence of KI. The dried precipitate was dissolved in 30 ml dimethylsulphoxide and diluted to 60 ml. The resulting solution was further diluted and the amount of bismuth was estimated spectrophotometrically at 360 nm and/or 420 nm using calibration curves prepared under similar conditions. Bismuth in the range 0.5-10 mg was precipitated with 10 ml 0.03M DMP and determined spectrophotometrically at 360 nm and/or 420 nm.

Results and Discussion

Table 1 contains the analytical data of the precipitate of Sb(III), Bi(III) and Hg(II) obtained from strongly acidic solution of the metal ions with DMP as precipitating agent in the presence of excess of KI. A large excess of KI is required to obtain the compounds. The final precipitates are thermally stable and are sparingly soluble in water. The formation of the final compound is very much dependent upon the amount of KI added. For example the weight of the precipitate obtained in the case of Bi(III) as a function of the concentration of KI is shown in Fig. 1. Three compounds, Bi(DMP)I₃, Bi(DMP)I₃.HI and Bi(DMP)I₃.2HI were obtained as a function of the iodide concentration. The latter two could be isolated in pure form. In the case of Hg(II) two compounds (DMP) HgI₂ and (DMP) HgI₂.2HI

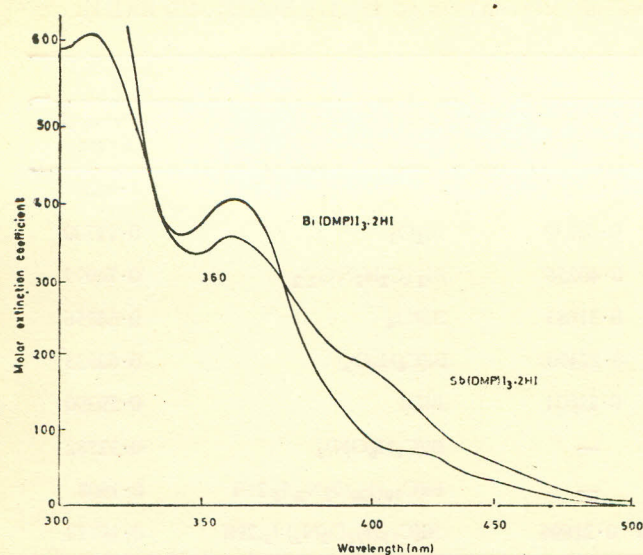


Fig. 3. Visible absorption spectra of $\text{Sb}(\text{DMP})\text{I}_3 \cdot 2\text{HI}$ and $\text{Bi}(\text{DMP})\text{I}_3 \cdot 2\text{HI}$ in dimethyl sulphoxide.

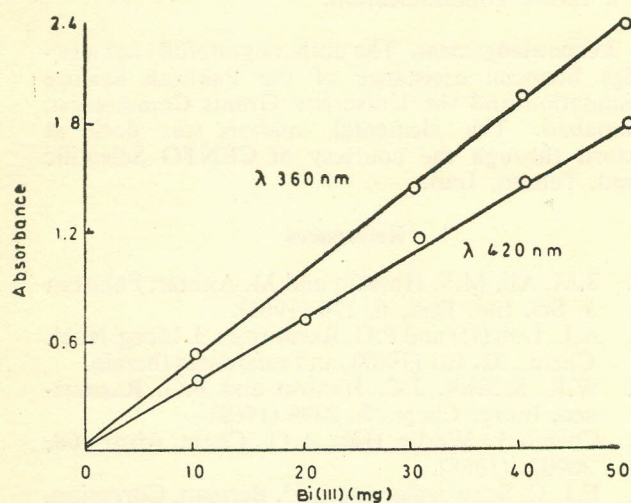


Fig. 4. Variation of absorption with 0-50 mg of $\text{Bi}(\text{III})$ at 360 and 420 nm.

TABLE 3. ESTIMATION OF $\text{Hg}(\text{III})$ USING DMP AS GRAVIMETRIC REAGENT.

Wt of $\text{Hg}(\text{II})$ (mg)	Found		Absolute deviation
	Wt of ppt (mg)	Calcd $\text{Hg}(\text{II})$ (mg)	
41.0	184.4	40.0	-1.0
82.0	368.8	80.0	-2.0
100.3	464.7	100.8	+0.5
120.6	553.2	120.0	-0.6
142.0	651.4	141.3	-0.7
177.0	807.7	175.2	-1.8
199.0	911.4	197.7	-1.3
212.0	969.9	210.4	-1.8
232.0	1062.6	230.5	-1.5

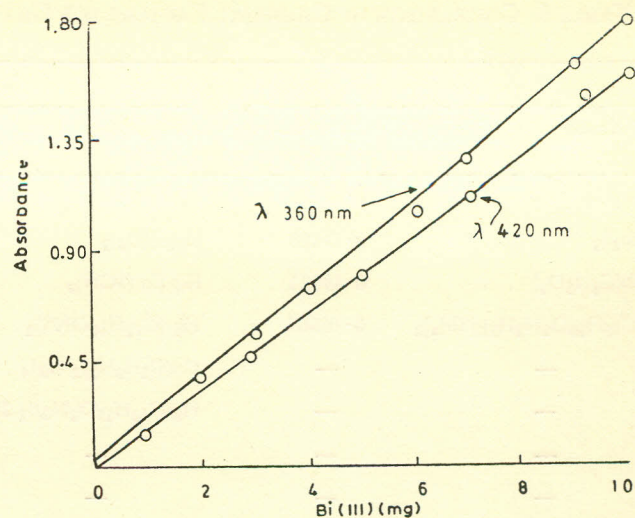


Fig. 5. Variation of absorption with 0-10 mg $\text{Bi}(\text{III})$ at 360 and 420 nm.

TABLE 4. ESTIMATION OF BISMUTH (III) USING DMP AS GRAVIMETRIC REAGENT.

Wt of Bi (mg)	Found		Absolute deviation
	Wt of ppt (mg)	Calcd Bi (mg)	
200	1.0140	199.9	-0.1
200	1.0150	200.1	+0.1
200	1.0135	199.8	-0.2
200	1.0160	200.3	+0.3
200	0.0121	199.6	-0.4
100	0.5068	99.9	-0.1
100	0.5080	100.2	+0.2

TABLE 5. SPECTROPHOTOMETRIC ESTIMATION OF BISMUTH(III) BELOW 50 mg USING 1,3-DIMORPHOLINOPROPANE.

Wavelength (nm)	Bi taken (mg)	Absorbance				Bismuth found (mg)
		I	II	III	Average	
360	25.0	1.15	1.14	1.15	1.15	24.8
420	30.0	1.08	1.09	1.07	1.086	30.5
360	3.0	0.52	0.53	0.53	0.53	2.95
420	4.0	0.65	0.66	0.66	0.66	4.10

were isolated in pure form whereas only $(\text{DMP})_2\text{SbI}_3 \cdot 2\text{HI}$ could be isolated in the case of $\text{Sb}(\text{III})$. The latter salt can be formulated as $[\text{C}_{11}\text{H}_{22}\text{O}_2\text{N}_2\text{H}_2][\text{SbI}_4]_2$. A plot of the weight of the precipitate as a function of iodide concentration (Fig. 2.) has a single plateau for $\text{Sb}(\text{III})$ compared to three in Fig. 1. for $\text{Bi}(\text{III})$. Preliminary experiments indicate that $\text{Sb}(\text{III})$ can be selectively estimated by this method even in the presence of arsenic and tin. A comparison of the calculated and estimated amounts of $\text{Sb}(\text{III})$, $\text{Bi}(\text{III})$

TABLE 6. COMPARISON OF CHEMICAL FACTORS FOR GRAVIMETRIC ESTIMATION OF Hg(II), Sb(III) AND Bi(III).

Sb(III)		Hg(II)		Bi(III)	
Weighed as	Chemical factor	Weighed as	Chemical factor	Weighed	Chemical factor
Sb ₂ O ₄	0.79188	HgS	0.86219	Bi	1.0000
Sb ₂ S ₃	0.71683	Hg ₅ (IO ₆) ₂	0.69230	Bi ₂ O ₃	0.89700
Sb(C ₆ H ₅ O ₃)	0.49322	Hg Zn (SCN) ₄	0.40256	Bi ₂ (C ₂ H ₃ NO ₂) ₂	0.74099
[C ₁₀ H ₂₀ O ₂ N ₂ H ₂][SbI ₄] ₂	0.16667	Hg(C ₁₂ H ₁₀ ONS) ₂	0.31683	BiPO ₄	0.68756
—	—	Cu(C ₂ H ₈ N ₂) ₂ HgI ₄	0.22490	Bi(C ₆ H ₃ O ₃)	0.62935
—	—	Hg(C ₁₀ H ₂₀ O ₂ N ₂) ₂ .2HI	0.22031	BiOI	0.59390
—	—	—	—	Bi(C ₉ H ₆ ON) ₃	0.32582
—	—	—	—	Bi(C ₁₀ H ₂₀ O ₂ N ₂) ₃ .2HI	0.1998
[C ₁₁ H ₂₂ O ₂ N ₂ H ₂][SbI ₄] ₂	0.16509	Hg(C ₂₂ H ₂₂ O ₂ N ₂) ₂ .2HI	0.21696	Bi(C ₁₁ H ₂₂ O ₂ N ₂) ₃ .2HI	0.19718

and Hg(II) is given in Tables 2-4. The errors in all the cases are within experimental limitations.

The direct gravimetric estimations of Bi(III) below 50 mg were not reproducible. Therefore, spectrophotometric procedures were used for estimation of Bi(III) in the range 0.5-50 mg. Bi(III)I₃.2HI is soluble in dimethyl sulphoxide and N,N'-dimethylformamide to give clear solutions having maxima at 360 nm (ϵ 400) and at 420 nm (ϵ 78) beside a strong maximum at 310 nm (ϵ 610) from ligand (Fig. 3). The amount of Bi(III) below 50 mg were estimated using DMSO solution of the bismuth compounds. Beer's law is obeyed for the amount of Bi(III) from 0.5 to 50 mg at both 360 and 420 nm. The amount of Bi(III) could be easily estimated from the calibration curves shown in Figs. 4 and 5. The high values of extinction coefficients at 350 and 420 nm permit the estimation of Bi(III) even below 0.5 mg. Results of some typical estimations of Bi(III) by spectrophotometric procedures are given in Table 5. The Hg(DMP)I₂.2HI and DMP.2SbI₃.2HI were also soluble in DMSO and N,N'-dimethylformamide. However, spectrophotometric estimation of Hg(II) and Sb(III) were not carried out and these ions were estimated to a lower limit of 25 mg using gravimetric procedures only.

A tabulation of chemical factors for gravimetric estimation of Sb(III), Hg(II) and Bi(III) given in Table 6 shows that the chemical factors for DMP as precipitating agent is minimum among the quantitative methods so far reported in the literature. The methods reported here permit excellent gravimetric determinations of Sb(III), Hg(II) and Bi(III) by forming sparingly soluble crystalline compounds which are easy to handle under normal laboratory conditions. The effect of interfering ions are being investigated to explore the feasibility of these procedure for estimating Sb(III), Hg(II) and Bi(III) in various complex materials. These results and

estimation of Zn(II) with DMP would be the subject of a future communication.

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