

Gravimetric Determination of Palladium, Silver, Mercury and Copper with 2-Mercaptomethylbenzimidazole

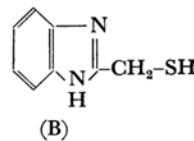
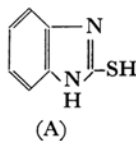
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New selective methods are described for the gravimetric determination of palladium, silver, copper and mercury with 2-mercaptomethylbenzimidazole. In the presence of EDTA or tartrate, palladium, silver and mercury are determined at pH of 4–5. Copper is determined as the copper(I) complex in the same pH range using cyanide as a reducing and complexing agent. Thermogravimetric studies reveal adequate thermal stability of the complexes. X-Ray studies confirm the identity of the end products in the thermolysis of the copper(I) and copper(II) complexes.

2-Mercaptobenzimidazole (A) is a widely used organic precipitant for cations,¹⁾ and has been employed in the gravimetric,²⁾ spectrophotometric,^{3,4)} amperometric⁵⁾ determination of palladium and spectrophotometric determination of osmium.⁶⁾ Though extensively used as an analytical reagent it is highly non-specific.⁷⁾ As part of an investigation on the analytical applications of some analogous heterocyclic thiols, 2-mercaptomethylbenzimidazole (B) was selected. As in this compound the thiol group is linked to the ring system through an additional carbon atom, it may form five-membered chelates with metal ions and may exhibit a greater degree of selectivity compared to (A). The compound forms chelates⁸⁾ with nickel and copper and has been used in the spectrophotometric determination⁹⁾ of palladium and in the amperometric titration¹⁰⁾ of palladium, silver and copper.



The present study shows that the reagent can be successfully utilised for the gravimetric determination of palladium, silver and mercury in the pH range of 4–5 by weighing their 1:2, 1:1 and 1:2 complexes respectively. Copper can be determined in the same pH range as the copper(I) complex, because the precipitate of the copper(II) complex is finely divided and is difficult to work with.

In the presence of tartrate or EDTA most of the common ions do not interfere in the determination of palladium, silver and mercury. Interferences of Pt^{4+} , Cu^{2+} , Ag^+ or Hg^{2+} in the determination of palladium are obviated by masking palladium with cyanide. Copper, silver and mercury interfere mutually. The selectivity for copper is achieved by using cyanide as a masking and reducing agent.

Thermogravimetric studies indicate that the complexes have adequate thermal stabilities. The complexes of palladium and silver are decomposed into metals. The mercury complex is converted into metallic mercury which finally escapes. The complexes of copper leave a residue which is a mixture of Cu(I) and Cu(II) oxides as confirmed by X-ray analysis.

Experimental

Apparatus. Measurements of pH were made with a Beckman model G pH meter. A Chevenard thermobalance of type 3 of ADAMEL¹¹⁾ (Paris) was used for thermal analysis. X-Ray studies were performed in

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1) F. J. Welcher, "Organic Analytical Reagents," Vol. IV, Van Nostrand, New York (1948), p. 127.

2) A. K. Majumdar and M. M. Chakrabarty, *Z. anal. Chem.*, **162**, 101 (1958).

3) J. Xavier, *ibid.*, **164**, 250 (1958).

4) A. K. Majumdar and M. M. Chakrabarty, *Anal. Chim. Acta*, **20**, 379 (1959).

5) A. K. Majumdar and M. M. Chakrabarty, *ibid.*, **20**, 386 (1959).

6) B. C. Bera and M. M. Chakrabarty, *Anal. Chem.*, **38**, 1419 (1966).

7) B. C. Bera and M. M. Chakrabarty, *Z. anal. Chem.*, **223**, 169 (1966).

8) G. K. Hughes and F. Lions, *J. Proc. Roy. Soc., (New South Wales)*, **71**, 209 (1937–1938).

9) B. C. Bera and M. M. Chakrabarty, *Mikrochim. Acta*, **1966**, 1094.

10) B. C. Bera and M. M. Chakrabarty, *Talanta*, **13**, 1186 (1966).

11) C. Duval, "Inorganic Thermogravimetric Analysis," 2nd Ed., Elsevier Publishing Co., Amsterdam (1963).

Siemens Krystalloflex-4 using copper target at 35 kV and 16 mA. The exposure time was 3 hr with a 114.6 mm dia. camera.

Reagent Solution. 2-Mercaptomethylbenzimidazole was prepared as described¹²⁾ and a 0.5% (W/V) solution in 50% (V/V) aqueous ethanol was employed.

Standard Solutions. Stock solutions of palladium, silver and mercury were prepared and standardised as described earlier.¹²⁾ For the standard solution of copper an accurately weighed amount of electrolytic copper (99.99% pure) was dissolved in nitric acid and the excess acid was expelled from the solution.

Preparation of the Complexes. Moderate excess of the reagent was added to the solution of metal ions, buffered with sodium acetate and acetic acid in the pH range of 4–5. The precipitates were allowed to settle, filtered, washed with water and dried in air. The palladium complex was yellow and the copper(II) complex was blue in colour. The other complexes were light yellow.

For preparation of the copper(I) complex, sufficient quantity of saturated sodium sulphite solution or 5% solution of an alkali cyanide was added to copper(II) solution and the pH of the solution was adjusted to 4–5. The solution was heated on the water bath and copper was precipitated as the yellow copper(I) complex. The precipitate was filtered, washed with hot water and dried in air.

Composition of the Complexes. The air dried complexes were dried at 110°C for at least 1 hr and were preserved in a desiccator. The sulphur contents

of all the complexes and the metal contents of the palladium, silver and mercury complexes were determined in the same way as reported earlier.¹²⁾

The copper(I and II) complexes were decomposed with concentrated nitric acid. Excess nitric acid and the oxides of nitrogen were expelled by carefully evaporating the solutions with concentrated sulphuric acid and copper was determined iodometrically.

The compositions were as follows:

Found: Pd, 24.56; S, 14.66%. Calcd for $\text{Pd}(\text{C}_8\text{H}_7\text{N}_2\text{S})_2$: Pd, 24.58; S, 14.85%. Found: Ag, 39.72; S, 11.70%. Calcd for $\text{Ag}(\text{C}_8\text{H}_7\text{N}_2\text{S})$: Ag, 39.80; S, 11.82%. Found: Hg, 37.80; S, 11.93%. Calcd for $\text{Hg}(\text{C}_8\text{H}_7\text{N}_2\text{S})_2$: Hg, 38.06; S, 12.17%. Found: Cu, 16.18; S, 16.26%. Calcd for $\text{Cu}(\text{C}_8\text{H}_7\text{N}_2\text{S})_2$: Cu, 16.30; S, 16.44%. Found: Cu, 28.10; S, 14.10%. Calcd for $\text{Cu}(\text{C}_8\text{H}_7\text{N}_2\text{S})$: Cu, 28.02; S, 14.14%.

Thermal Studies of the Reagent and the Complexes. Aliquots (50–100 mg) of the reagent and the complexes were separately taken in a micro crucible and heated in the thermobalance at the rate of 5°C per minute. The thermogravimetric analysis curves are shown in Fig. 1.

The reagent started decomposing around 170°C and the destruction of the organic matter continued till 620°C, when the crucible was empty.

The palladium complex remained stable up to 200°C, thereafter underwent slow decomposition till 410°C. Above this point the decomposition was rapid and the level of metallic palladium appeared near 500°C.

The silver complex was stable up to 165°C, then

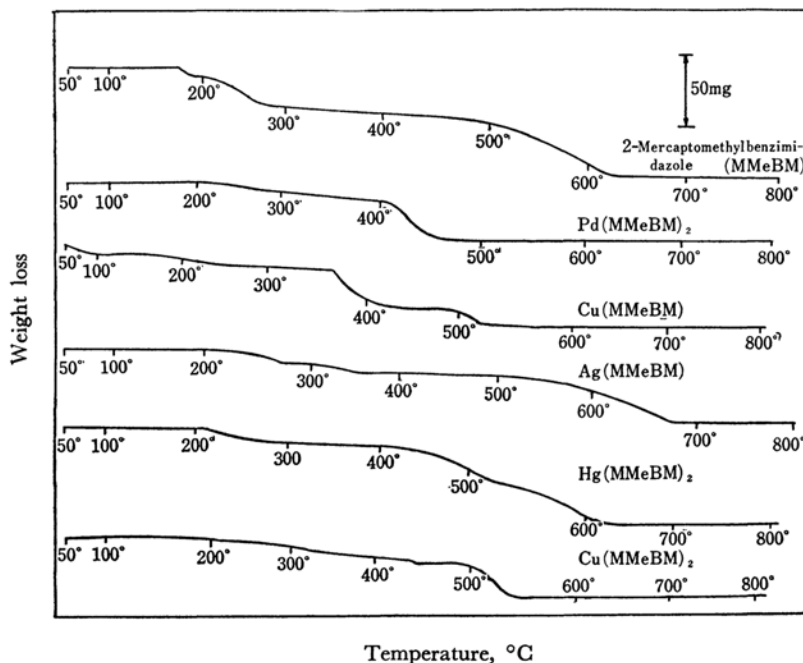


Fig. 1. Thermogravimetric analysis curves.

12) B. C. Bera and M. M. Chakrabartty, *Indian J. Appl. Chem.*, **29**, 75 (1966).

TABLE 1. EFFECT OF pH ON THE DETERMINATION OF PALLADIUM, SILVER, MERCURY AND COPPER

Pd taken = 12.70 mg, Ag taken = 31.40 mg, Hg taken = 38.14 mg, Cu taken = 20.54 mg

Wt. of Pd ppt. (mg)	Pd found (mg)	Wt. of Ag ppt. (mg)	Ag found (mg)	Wt. of Hg ppt. (mg)	Hg found (mg)	Wt. of Cu (I) ppt. (mg)	Cu found (mg)	pH
48.6	11.95	73.2	29.14	90.0	34.26	66.5	18.63	2.0
50.0	12.29	74.6	29.69	95.0	36.31	68.7	19.25	3.0
50.2	12.33	76.6	30.48	89.0	37.25	70.8	19.84	3.5
50.8	12.48	77.4	30.80	98.8	37.61	71.8	20.12	3.7
51.4	12.64	78.6	31.28	99.7	37.95	73.0	20.46	4.0
51.8	12.74	78.7	31.32	100.2	38.15	73.0	20.46	4.3
52.0	12.78	79.0	31.45	100.2	38.15	73.3	20.54	4.5
52.0	12.78	79.2	31.52	100.5	38.23	73.3	20.54	4.8
52.1	12.80	79.2	31.52	100.7	38.31	73.6	20.63	5.0
52.4	12.88	80.0	31.83	101.4	38.60	74.3	20.81	5.2
53.2	13.10	82.4	32.79	102.4	38.97	75.8	21.24	5.5
53.8	13.26	84.6	33.65	104.0	39.60	77.0	21.58	6.0
55.0	13.52	86.2	34.30	106.5	40.53	79.5	22.28	8.0
57.0	14.01	88.5	35.22	109.0	41.48	82.7	23.17	10.0

decomposed slowly till 500°C and rapidly thereafter till 658°C where the horizontal due to metallic silver appeared.

The mercury complex began to lose weight slowly above 180°C till about 400°C when the rate became rapid and the crucible was empty at 640°C. Probably around 400°C mercury was set free from the complex and the rapid loss in weight was due to the escape of mercury and destruction of organic matter.

The initial slope in the T.G.A. profile of the copper(II) complex was due to the loss of adsorbed moisture. The short horizontal of 105–130°C was due to the diligand complex. The decomposition over the range fo 130–577°C appeared stepwise but there was no strict horizontal. The residue was a mixture of copper(I and II) oxides as confirmed by X-ray studies.

The copper(I) complex was stable up to 170°C, then slowly decomposed till 500°C. Above this point, the rate of decomposition was rapid and a horizontal appeared at 560°C. The residue was again a mixture of the two oxides of copper.

The limiting temperatures of the initial horizontals in the respective thermograms exhibit a decreasing order, such as, Pd(200°C) > Hg(180°C) > Cu^I(170°C) > Ag(165°C). This may be taken to be a rough order of the relative thermal stabilities of the complexes. Properties, such as, ionic radii¹³⁾ or atomic weights of the metals do not conform to such an order. However, the "ionic potentials" (the ratio of charge to ionic radius) decrease in the order Pd²⁺ > Hg²⁺ > Cu⁺ > Ag⁺ which is in agreement with the above sequence of thermal stability. But the exclusion of the copper(II) complex is not clear. Though the "ionic potential" of Cu²⁺ is higher than that of Hg²⁺, the complex exhibits the least thermal stability.

Procedure for Palladium, Silver and Mercury. Sufficient amount of 10% (W/V) EDTA. (disodium salt) or tartaric acid solution was added to the solution

of a metal ion. The solution was made just alkaline, diluted to about 150 ml and the pH was adjusted to 4–5 by adding dilute sodium hydroxide or acetic acid. Moderate excess of the reagent was added with stirring. The precipitates was allowed to settle, filtered through a weighed gooch crucible (G₃ or G₄), washed with hot water (the mercury precipitate was washed with cold water), dried at 110°C and weighed. The results are recorded in Table 1.

Procedure for Copper. To an aliquot of the copper (II) solution 5 ml of 5% sodium or potassium cyanide solution was added and the pH was adjusted as usual. The solution was heated to around 70°C on a water bath, copper was precipitated and the mixture was left on the water bath for 10–15 min. The precipitate was filtered, washed with hot water, dried at 110°C and weighed. The results are shown in Table 1.

The metal ions were quantitatively precipitated in the pH range of 4–10, but the precipitates conformed to the above formulas at a pH 4–5. The high results beyond this range were due to the insolubility of the reagent while the values at lower pH were due to the solubility of the complexes.

The reagent not being very soluble a large excess of it was avoided. Generally, 10 ml of the reagent solution was sufficient for complete precipitation of 10 mg of palladium or copper and 20 mg of silver or mercury.

Effect of Diverse Ions. Excess EDTA or tartrate solution was added to the palladium, silver or mercury solution containing the diverse ions. The volume of the solution was made to 150 ml and the pH was adjusted to 4–5. The metal ions were precipitated with the requisite amount of the reagent. The precipitates were filtered, dried and weighed as usual. Interferences of Pt⁴⁺, Cu²⁺, Ag⁺ and Hg²⁺ in the determination of palladium were obviated by complexing palladium with cyanide and precipitating the above ions with the reagent. The filtrate was then evaporated carefully to decompose the cyanide. After complete removal of the cyanide as detected by the copper acetate-benzidine

13) L. E. Sutton, Ed., "Tables of Interionic Distances and Configuration of Molecules and Ions," Chemical Society, London (1958).

acetate reagent,¹⁴⁾ palladium was determined in the solution as usual. Copper, silver and mercury interfered mutually. Effects of diverse ions are presented in Tables 2—5.

TABLE 2. EFFECT OF DIVERSE IONS ON THE DETERMINATION OF PALLADIUM

Pd taken (mg)	Ions added	Amount added (mg)	Wt. of Pd ppt. (mg)	Pd found (mg)
12.70	Pt ⁴⁺	41.5	52.3	12.86
12.70	Ag ⁺	31.4	52.1	12.80
12.70	Hg ²⁺	38.1	52.2	12.83
12.70	Cu ²⁺	41.0	52.2	12.83
12.70	Pb ²⁺ , Cd ²⁺	40 each	51.8	12.74
12.70	Pb ²⁺ , Cd ²⁺	60 each	52.2	12.83
15.24	Mn ²⁺ , Zn ²⁺ , Mg ²⁺	40 each	62.1	15.26
15.24	Mn ²⁺ , Zn ²⁺ , Mg ²⁺	80 each	62.7	15.41
15.24	Co ²⁺ , Ni ²⁺	50 each	61.8	15.19
15.24	Co ²⁺ , Ni ²⁺	100 each	62.6	15.39
19.05	Ca ²⁺ , Sr ²⁺ , Ba ²⁺	50 each	77.3	19.00
19.05	Ca ²⁺ , Sr ²⁺ , Ba ²⁺	100 each	78.1	19.20
12.70	Fe ³⁺ , Cr ³⁺	50 each	52.2	12.83
19.05	Al ³⁺ , Be ²⁺ , Ti ⁴⁺	40 each	77.5	19.07
19.05	Al ³⁺ , Be ²⁺ , Ti ⁴⁺	80 each	78.4	19.27
15.24	Th ⁴⁺ , Zr ⁴⁺ , UO ₂ ²⁺	40 each	62.6	15.39
12.70	As ³⁺ , Sb ³⁺ , Bi ³⁺	50 each	52.1	12.80
12.70	Mo ⁶⁺ , V ⁵⁺	40 each	51.4	12.64

TABLE 3. EFFECT OF DIVERSE IONS ON THE DETERMINATION OF SILVER

Ag taken (mg)	Ions added	Amount added (mg)	Wt. of Ag ppt. (mg)	Ag found
31.40	Pd ²⁺	30.48	78.6	31.28
31.40	Pb ²⁺ , Cd ²⁺	60 each	79.1	31.48
31.40	Pb ²⁺ , Cd ²⁺	120 each	79.7	31.73
31.40	Mn ²⁺ , Zn ²⁺ , Mg ²⁺	60 each	78.9	31.41
31.40	Mn ²⁺ , Zn ²⁺ , Mg ²⁺	120 each	79.3	31.56
47.25	Co ²⁺ , Ni ²⁺	80 each	118.9	47.33
47.25	Co ²⁺ , Ni ²⁺	120 each	119.5	47.55
31.40	Ca ²⁺ , Sr ²⁺ , Ba ²⁺	60 each	79.1	31.48
31.40	Ca ²⁺ , Sr ²⁺ , Ba ²⁺	120 each	79.5	31.64
47.25	Fe ³⁺ , Cr ³⁺	80 each	119.7	47.61
31.40	Al ³⁺ , Be ²⁺ , Ti ⁴⁺	80 each	79.6	31.66
31.40	Th ⁴⁺ , Zr ⁴⁺ , UO ₂ ²⁺	50 each	79.3	31.56
31.40	As ³⁺ , Sb ³⁺ , Bi ³⁺	06 each	79.6	31.66
47.25	Mo ⁶⁺ , V ⁵⁺	80 each	119.5	47.55

TABLE 4. EFFECT OF DIVERSE IONS ON THE DETERMINATION OF MERCURY

Hg taken (mg)	Ions added	Amount added (mg)	Wt. of Hg ppt. (mg)	Hg found (mg)
19.07	Pb ²⁺ , Cd ²⁺	60 each	50.4	19.18
19.07	Pb ²⁺ , Cd ²⁺	90 each	50.5	19.23
19.07	Mn ²⁺ , Zn ²⁺ , Mg ²⁺	50 each	50.2	19.11
19.07	Mn ²⁺ , Zn ²⁺ , Mg ²⁺	100 each	50.5	19.23
38.14	Co ²⁺ , Ni ²⁺	80 each	100.4	38.21
38.14	Co ²⁺ , Ni ²⁺	120 each	100.7	38.32
38.14	Ca ²⁺ , Ba ²⁺ , Sr ²⁺	60 each	100.4	38.31
38.14	Ca ²⁺ , Ba ²⁺ , Sr ²⁺	120 each	100.7	38.32
19.07	Fe ³⁺ , Cr ³⁺	80 each	50.6	19.26
45.77	Al ³⁺ , Be ²⁺ , Ti ⁴⁺	80 each	120.6	45.88
19.07	Th ⁴⁺ , Zr ⁴⁺ , UO ₂ ²⁺	50 each	50.4	19.18
38.14	As ³⁺ , Sb ³⁺ , Bi ³⁺	60 each	100.7	38.32
19.07	Mo ⁶⁺ , V ⁵⁺	60 each	50.5	19.23

TABLE 5. EFFECT OF DIVERSE IONS ON THE DETERMINATION OF COPPER

Cu taken (mg)	Ions added	Amount added (mg)	Wt. of Cu ppt. (mg)	Cu found (mg)
20.54	Pb ²⁺ , Cd ²⁺	80 each	73.6	20.60
20.54	Pb ²⁺ , Cd ²⁺	160 each	74.0	20.73
30.81	Mn ²⁺ , Zn ²⁺ , Mg ²⁺	100 each	110.0	30.82
30.81	Mn ²⁺ , Zn ²⁺ , Mg ²⁺	150 each	110.5	30.96
30.81	Co ²⁺ , Ni ²⁺	100 each	110.0	30.82
30.81	Co ²⁺ , Ni ²⁺	150 each	110.6	30.96
30.81	Ca ²⁺ , Sr ²⁺ , Ba ²⁺	150 each	110.6	30.95
20.54	Fe ³⁺ , Cr ³⁺	80 each	73.7	20.65
41.08	Al ³⁺ , Be ²⁺ , Ti ⁴⁺	150 each	147.0	41.19
20.54	Th ⁴⁺ , Zr ⁴⁺ , UO ₂ ²⁺	50 each	73.5	20.60
20.54	As ³⁺ , Sb ³⁺ , Bi ³⁺	80 each	73.8	20.68
20.54	Mo ⁶⁺ , V ⁵⁺	60 each	73.6	20.63

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14) F. Feigl, "Qualitative Analysis by Spot Tests," 5th Ed., Elsevier Publishing Co., New York (1958), p. 276.