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# Bismuthiol II as an Analytical Reagent

## Part V\*

**Estimation of Silver** 

## By

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### With 1 Figure in the text

### (Eingegangen am 3. Oktober 1956)

Bismuthiol II reagent has been used by MAJUMDAR<sup>2</sup> for the colorimetric and gravimetric determination of bismuth. PANCHOUT<sup>5</sup> et al. in their thermogravimetric studies on the complexes of bismuth observe a high degree of stability of bismuth-Bismuthiol II complex and confirm that bismuth estimation by the reagent is highly satisfactory. MAJUMDAR and CHAKRABARTTY<sup>3</sup> have shown how the reagent has helped in the estimation of bismuth, palladium and platinum and their separations from each other as well from almost all other ions. Recently it has been found to be very effective for the estimation and separation of lead from a majority of the ions though Ag, Au<sup>3+</sup>, Hg, Tl, Cd and platinum metals, except palladium, interfere<sup>4</sup>.

The object of the present investigation is to study the composition and thermal stability of the silver-Bismuthiol II complex and the use of the reagent for the estimation of silver and its separation from diverse ions. It may be mentioned that WATT and BOYD<sup>6</sup> in thier studies on the preparation of metal salts with 2-mercapto-4-phenyl- $\Delta^2$ -1,3,4-thiodiazoline-5-thione, Bismuthiol(II), observed that the reagent formed two salts with mercury (II) and one each with Cu<sup>2+</sup>, Ni<sup>2+</sup> and Ag<sup>+</sup>. They found the silver complex to be yellow, having the composition C<sub>8</sub>H<sub>5</sub>N<sub>2</sub>S<sub>3</sub>Ag, which they reported to be decomposed by light, air and on heating to 150° C.

We find, on the other hand, that the silver complex formed by the reagent from a neutral or ammoniacal solution is yellow and though stable both in light and air, changes on heating to a black compound. But when the complex is formed from a neutral solution in presence of ammonium nitrate, it is stable in light, heat and air. The reagent prepared by us after three crystallisations from alcohol in presence of active charcoal has been found to melt at  $248^{\circ}$  C (WATT and BOYD,  $245^{\circ}$  C; BUSCH<sup>1</sup>,  $240^{\circ}$  C).

<sup>\*</sup> Part IV see Z. analyt. Chem. 155, 7 (1957).

Z. anal. Chem., Bd. 155

The potassium salt of the reagent precipitates silver completely in solutions of nitric acid up to a maximum acidity of about 0.2 N, sulphuric acid, acetic acid or ammonia up to about 1 N and in presence of citrate, tartrate, complexone III (di-sodium salt of ethylenediamine tetra acetic acid) and cyanide. The method for the precipitation of silver is found to be very simple, accurate and well applicable for its separation from almost all ions. For most of the separations, either complexone III or tartrate is used to mask the effect of the interfering ions. Tartrate however reduces silver at a high  $p_{\rm H}$  and so, whenever for the separation,  $p_{\rm H}$  adjustment over 7 is necessary, citrate is used to replace tartrate and the precipitation is done at a temperature of about 50–60° C.

As the reagent does not precipitate elements other than those of the sulphide group in 0.1 N nitric acid solution, silver is separated from alkalis, alkaline earths, rare earths ( $R_2O_3$ ), Be, Mg, Zn, Mn, Co, Ni, Cr, Al, Ce<sup>3+</sup>, Ti, Zr, Th,  $UO_2^{2^+}$ ,  $PO_4^{3^-}$  and  $AsO_4^{3^-}$ .

At a  $p_H$  between 5 and 9 besides the above ions the following ions in presence of a tartrate or a citrate are found not to interfere. The ions are Fe<sup>3+</sup>, Ce<sup>4+</sup>, As<sup>3+</sup>, Sb<sup>3+</sup>, Sn<sup>4+</sup>, Bi<sup>3+</sup>, MoO<sub>4</sub><sup>2-</sup>, WO<sub>4</sub><sup>2-</sup>, VO<sub>3</sub><sup>-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup>.

Similarly complexone III at the same  $p_{\rm H}$  (5—9) helps in the separation of silver from all the mentioned ions except Sn<sup>4+</sup> and including Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cd, Tl<sup>+</sup> and CrO<sub>4</sub><sup>2-</sup>. Mercury (I and II), Pt<sup>4+</sup>, Pd<sup>2+</sup>, Au<sup>3+</sup> and iodide interfere. Interfering effect of Sn<sup>4+</sup> can be avoided if tartrate is used along with complexone III as complexing agent. Separation from Pd<sup>2+</sup> can be done in presence of cyanide and from Au<sup>3+</sup> with thiosulphate. Estimation and separation of silver from precious metals will be the subject matter of a subsequent paper.

Undoubtedly the variety of conditions of precipitation of silver from high acidity to high  $p_{\rm H}$  in presence of various buffers and sequestering agents, combined with their simplicity without affecting the accuracy of the results, leave no doubt to rank this method as one of the best methods for the estimation of silver.

## **Experimental**

Reagents and apparatus. The potassium salt of the reagent Bismuthiol II was prepared according to the method of  $BUSCH^1$  and was recrystallised from alcohol. In this work a 0.5% aqueous solution of potassium salt of the reagent of m.p. 248° C was used.

Chemicals used were of highest purity available. A standard solution of silver was prepared from A.R. B.D.H. sample of silver nitrate and its strength was determined gravimetrically as chloride. Solutions of other cations were prepared from their nitrates or sulphates and those of anions from their sodium or potassium salts, and the strength of the solutions was determined by standard procedures. Rare earth solution free from thorium was prepared from monazite sand.

 $p_{\rm H}$  determinations were carried out by a Bench model  $p_{\rm H}$ -meter.

## Composition and thermal Stability of Silver-Bismuthiol II Complex

A solution of silver nitrate containing 1-2 g of ammonium nitrate and a few drops of dilute nitric acid was warmed to  $60-70^{\circ}$  C and precipitated with the reagent solution. The precipitate was filtered, washed and dried in air.

From the air-dried sample of silver complex, the components, silver and sulphur were determined as silver chloride and barium sulphate respectively after the decomposition of the complex according to the procedure referred to in a previous communication<sup>4</sup>.



Fig. 1. Thermolysis curve of silver complex

The silver-Bismuthiol II complex was found to have the composition  $C_8H_5N_2S_3Ag$  (% Ag calc. 32.38; found 32.47; % S calc. 28.87; found 28.45) and from the thermolysis curve the complex was observed to maintain its composition up to a temperature of about 280° C (see thermolysis curve; Fig. 1).

#### Procedure

Estimation of silver. A silver nitrate solution (31.75 mg Ag) was acidified with dilute nitric, sulphuric or glacial acetic acid or made ammoniacal with ammonia (sp. gr. 0.888) and added to it 1—2 g of ammonium nitrate, diluted to a volume of 125 ml, warmed to 60—70° C and treated with the reagent solution dropwise with stirring till the precipitation was complete. A slight excess (3—4 ml) of the reagent solution was required. At higher acidity, than  $p_H 2$ , addition of ammonium nitrate was not necessary and there the temperature of the solution was maintained below 50° C, while the presence of much excess of the reagent was avoided to prevent unnecessary decomposition of the reagent by the free acid. The precipitate was filtered through a weighed GOOCH crucible, washed with hot water, and weighed after drying in an air oven at 110—120° C.

The weight of the silver complex when multiplied by the factor 0.3238 gave the silver content (see Table 1, p.84).

During the separation of silver from interfering ions usually citrate, tartrate or complexone III was used as the masking agent and the  $p_{\rm H}$  of the solution was adjusted anywhere between 2 and 9 according to

the requirements and the procedure followed was exactly the same as stated above. The  $p_{\rm H}$  above 5 was usually adjusted by dilute ammonia.

When cyanide was used as the masking agent the  $p_{\rm H}$  of the solution was maintained at 5—6, the reagent added was 6—7 ml in excess and the mixture required boiling for about 8—10 minutes to decompose the silver cyanide complex that might form and prevent the complete precipitation of silver.

Nitric acid	Sulphuric acid	Acetic acid ml	Ammonia ml	Wt. of Ag complex mg	Ag found mg	рн
_	_			98.0	31.74	5.8
0.01 N				98.2	31.80	1.9
0.1 N			_	98.0	31.74	
0.2 N				97.6	31.60	—
0.3 N			~	95.8	31.02	
	0.01 N			98.2	31.80	1.9
	$0.1 \ \mathrm{N}$			98.4	31.86	—
	$0.5~{ m N}$			98.6	31.93	
_	I N			98.8	32.00	_
_	—	1		98.0	31.74	2.7
		5		97.6	31.60	2.4
		10		96.0	31.09	2.3
		/	2.5	97.8	31.66	9.4
			5.0	97.2	31.48	9.7

Table 1	
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## Estimation and separation of silver in 0.1 N acid or by control of $p_{\rm H}$

Silver was estimated in presence of the ions  $Be^{2+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Zn^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cr^{3+}$ ,  $Al^{3+}$ ,  $Ce^{3+}$ , rare earths,  $Ti^{4+}$ ,  $Zr^{4+}$ ,  $Th^{4+}$ ,  $UO_2^{2+}$ ,  $AsO_4^{3-}$  and  $PO_4^{3-}$  from a solution whose acidity was maintained at 0.1 N in nitric acid (see Table 2).

Ions added		Wt. of ppt. mg	Ag found mg	Ions added	Wt. of ppt. mg	Ag found mg
${{ m Mg^{2+}}\atop{{ m Ca^{2+}}}}$	$\left. \begin{array}{c} \mathrm{Sr}^{2+} \\ \mathrm{Ba}^{2+} \end{array} \right\}$	98.4	31.86	$\left. \begin{array}{c} \mathrm{Cr}^{3+} \\ \mathrm{Al}^{3+} \end{array} \right\}$	98.2	31.80
1				$Ce^{3+}$	98.4	31.86
				$R_2O_3$	98.6	31.93
$Be^{2+}$		98.4	31.86	$Ti^{4+}$	98.6	31.93
$Zn^{2+}$		98.6	31.93	Zr <sup>4+</sup>	98.4	31.86
${ m Mn^{2+}}\ { m Co^{2+}}$	$Ni^{2+}$	98.0	31.74	$\left. egin{array}{c} { m Th^{4+}} \\ { m UO_2^{2+}} \end{array}  ight\}$	98.4	31.86
				$\left. \begin{array}{c} \mathrm{PO_4^{3-}} \\ \mathrm{AsO_4^{3-}} \end{array} \right\}$	98.4	31.86

Table 2. Silver taken, 31.75 mg and each interfering ion, 250 mg

Separation of silver from alkaline earths,  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $AsO_4^{3-}$ ,  $PO_4^{3-}$  and  $C_2O_4^{2-}$  was done also at a  $p_H$  adjusted between 6 and 8 in presence of an excess of ammonium nitrate (5 g).

In presence of tartaric acid (5 g) separation from Fe<sup>3+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>, Be<sup>2+</sup>, As<sup>3+</sup>, Sb<sup>3+</sup>, Sn<sup>4+</sup>, Ti<sup>4+</sup>, Zr<sup>4+</sup>, Th<sup>4+</sup>, UO<sub>2</sub><sup>2+</sup>, MoO<sub>4</sub><sup>2-</sup>, WO<sub>4</sub><sup>2-</sup> and VO<sub>3</sub><sup>-</sup> was achieved at a  $p_{\rm H}$  between 5 and 7 (see Table 3).

Ions of Ce<sup>3+</sup>, Ce<sup>4+</sup>, Bi<sup>3+</sup> and of rare earths were easily separated in presence of citric acid (4 g) at a  $p_{\rm H}$  between 6 and 9 (see Table 3).

With complexone III, 3—5 g, as the complexing agent, silver was estimated in presence of the ions of alkalis, alkaline earths, rare earths, Be<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Bi<sup>3+</sup>, As<sup>3+</sup>, Sb<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup>, Ce<sup>3+</sup>, Ce<sup>4+</sup>, Ti<sup>4+</sup>, Zr<sup>4+</sup>, Th<sup>4+</sup>, UO<sub>2</sub><sup>2+</sup>, Sn<sup>4+</sup>, Tl<sup>+</sup>; PO<sub>4</sub><sup>3-</sup>, AsO<sub>4</sub><sup>3-</sup>, MoO<sub>4</sub><sup>2-</sup>, WO<sub>4</sub><sup>2-</sup>, VO<sub>3</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup> when the p<sub>H</sub> of the solution was 5—7. Tl<sup>+</sup> of course required the maintenance of p<sub>H</sub> at 8–9 (see Table 3).

Ions	added mg	Wt. of ppt. mg	Ag found mg	Ions	added mg	Wt. of ppt. mg	Ag found mg
Be <sup>2+</sup>	200]	08.9	21 20	Ce <sup>3+</sup>	200	98.2	31.80
$Mg^{2+}$	200∫	30.2	31.00	$Ce^{4+}$	200	98.4	31.86
$Zn^{2+}$	100)			$R_2O_3$	200	98.4	31.86
$Mn^{2+}$	100			Ti <sup>4+</sup>	200	98.4	31.86
$Co^{2+}$	100	98.4	31.86	Zr <sup>4+</sup>	200	98.4	31.86
Ni <sup>2+</sup>	100			Th4+	2001		
211	100)			$\overline{\mathrm{UO}}_{2^+}$	200	98.6	31.93
$\mathrm{Pb^{2+}}$ .	250	98.6	31.93		-00j		
$Cu^{2+}$	250	98.4	31.86	$PO_4^{3-}$	250	98.0	31.74
$Cd^{2+}$	250	98.6	31.93	$AsO_4^{3-}$	250	98.0	31.74
Bi <sup>3+</sup>	250	98.4	31.86	MoO <sub>4</sub> <sup>2</sup>	250	98.0	31.74
	2202			WO4 <sup>2-</sup>	250	98.2	31.80
$As^{3+}$	250	98.6	31.93	VO <sub>3</sub> -	250	98.2	31.80
$Sb^{3+}$	250J	20.0	01.00	CrO <sub>4</sub> <sup>2-</sup>	250	98.2	31.80
$\mathrm{Fe}^{3+}$	200)			$Tl^+$	200	98.8	32.00
$\operatorname{Cr}^{3+}$	200	98.4	31.86	T1+	250	99.4	32.19
$Al^{3+}$	200J			Sn <sup>4+</sup>	250	98.6	31.93

Table 3. Silver taken, 31.75 mg

## Summary

Silver was estimated from a solution of high acidity to high  $p_{\rm H}$  as its Bismuthiol II complex having the composition  $C_8H_5N_2S_3Ag$ . The precipitate was found to be quite stable towards heat and light; the thermolysis curve showed the silver complex to be stable up to about 280°C. With the reagent silver could be estimated in presence of nitric acid up to a maximum acidity of about 0.2 N, sulphuric acid, acetic acid and ammonia up to about 1 N and also in presence of complexone III, citrate, tartrate and cyanide. With Complexone III, silver could be separated at a  $p_H$  between 5 and 9 from almost all ions except Hg<sup>+</sup>, Hg<sup>2+</sup>, Pt<sup>4+</sup>, Pd<sup>2+</sup> and Au<sup>3+</sup>; the latter two could however be separated with cyanide and thiosulphate respectively as the complexing agents.

## References

<sup>1</sup> BUSCH, M.: Ber. dtsch. chem. Ges. 27, 2510 (1894). — <sup>2</sup> MAJUMDAR, A.K.: J. Indian chem. Soc. 19, 396 (1942); 21, 347 (1944). — <sup>3</sup> MAJUMDAR, A.K., and M. M. CHAKRABARTTY: Z. analyt. Chem. 154, 262 (1957); 155, 1, 7 (1957). — <sup>4</sup> MAJUMDAR, A. K., and B. R. SINGH: Z. analyt. Chem. 154, 413 (1957). — <sup>5</sup> PAN-CHOUT, S., and CL. DUVAL: Anal. chim. Acta 5, 170 (1951). — <sup>6</sup> WATT, G. W., and M. E. BOYD: J. Amer. chem. Soc. 69, 185 (1947).

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## **Bismuthiol II as an Analytical Reagent**

## Part VI\*

Estimation of Thallium (I)

By

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With 1 Figure in the text

## (Eingegangen am 3. Oktober 1956)

MAJUMDAR and Coworkers<sup>1, 2, 3</sup> in their systematic quantitative studies on the behaviour of ions towards Bismuthiol II observed the reagent to give a bright yellow precipitate with thallous ion while thallic oxidized the reagent. Unlike other Bismuthiol II complexes thallous-complex showed increased solubility in hot solution, specially in presence of complexone III (disodium salt of ethylene diamine tetra acetic acid) at higher  $p_{\rm H}$  regions and an extraordinary stability towards cyanide in the alkaline range. It was felt of great interest if thallous estimation with this reagent could be made by suppressing the solubility of the thallous complex with the use of an excess of the reagent combined with the cooling of the precipitate before filtration.

The object of this paper is to present the composition, stability, quantitative nature of precipitation of thallous with Bismuthiol II reagent and the method of its separation from almost all ions.

Thallous precipitation is found to be quantitative if 8—10 ml excess of the reagent than the required amount are added to the warm solution (50—60° C) and the precipitate suddenly cooled to about  $10^{\circ}$  C before filtration. The results obtained thereby agree well with those due to

<sup>\*</sup> Part V see Z. analyt. Chem. 155, 81 (1957).