

THERMOGRAVIMETRIC ANALYSIS OF SOME
METAL THIOCARBONATES AND SULPHIDES OBTAINED WITH
POTASSIUM THIOCARBONATE (PTC) REAGENT

K. N. JOHRI, N. K. KAUSHIK and K. SINGH

Department of Chemistry, University of Delhi, Delhi-7, India

(Received November 3, 1969)

The thiocarbonates of K(I), Tl(I), Pb(II), Cd(II), Cu(II), Co(II), Ni(II), Zn(II), Fe(II) and the sulphides of Ag(I), Cu(II), Cd(II), Hg(II), Bi(III), Mo(VI), Pt(IV), Au(III), V(V), Se(IV), Te(IV), As(III, V), Sb(III) have been studied by thermogravimetric analysis. These studies not only confirm the purity of the precipitated products obtained with PTC but also determine correct temperature ranges for the precipitates to attain constant weight, thereby affording gravimetric evaluations of even mg quantities of the metal ions studied. Purity of precipitated products was made possible with the technique of precipitation from homogeneous solution based on the PTC reagent as precipitant.

Analytical applications of potassium thiocarbonate (PTC) reagent as a source of sulphide and thiocarbonate ions within solution, replacing the gaseous hydrogen sulphide, have been studied extensively in the qualitative [1—8] and quantitative [9—14] analysis of metal ions as reported earlier. The present communication includes TG studies [15, 16] of thiocarbonates of potassium(I), thallium(I), lead(II), copper(II), cadmium(II), iron(II), cobalt(II), nickel(II) and zinc(II) and sulphides of silver(I), copper(II), cadmium(II), molybdenum(VI), lead(II), platinum(IV), gold(III), mercury(II), vanadium(V), selenium(IV), tellurium(IV), arsenic(III, V), antimony(III) and bismuth(III). Such a study of metal thiocarbonates and metal sulphides obtained with PTC has not been carried out as gathered from the literature [17]. This may be attributed to the difficulties met in isolating pure thiocarbonates. TG studies of solid potassium thiocarbonate [18] and thallos thiocarbonate [19] have already been reported from these laboratories. In the present study, optimum conditions for the clean precipitation of other metal thiocarbonates and sulphides have been worked out with a view to determine:

- (i) the ranges of temperature for the different stages of transformation of the metal thio-compounds affording standardization of the conditions of their quantitative estimation as thiocarbonates, sulphides, sulphates or oxides by weighing;
- (ii) any deviations from the stoichiometric compositions of the precipitated products, thereby establishing the extent of purity of the metal thiocarbonates or sulphides;

Table 1
Preparatory methods for metal thiocarbonates and sulphides

No.	Compound	Colour of the compound	Salt of metal taken	Strength of PTC used	Conditions for precipitating the compound	References
1.	Potassium thiocarbonate (K_2CS_3)	Orange	KOH	2 M	Solid PTC was obtained by evaporating the aq. soln. under reduced pressure at 30 °C	18, 21
2.	Thallous thiocarbonate (Tl_2CS_2)	Vermilion	$TlNO_3$	0.1 M	Precipitated from aqueous solution	12, 20
3.	Lead thiocarbonate ($PbCS_3$)	Red	$Pb(NO_3)_2$	0.1 M	Obtained by adding PTC to metal-EDTA complex in alkaline medium by cation generation technique	15, 22
4.	Cadmium thiocarbonate ($CdCS_3$)	Yellow	$Cd(NO_3)_2$	0.1 M		
5.	Copper thiocarbonate ($CuCS_3$)	Chocolate-brown	$CuSO_4 \cdot 5H_2O$	0.1 M		
6.	Cobalt thiocarbonate ($CoCS_3$)	Greenish-black	$Co(NO_3)_2 \cdot 6H_2O$	0.1 M		
7.	Nickel thiocarbonate ($NiCS_3$)	Pinkish-red	$Ni(NO_3)_2$	0.1 M	Obtained by adding PTC to metal ammine complexes till the precipitation was complete and the supernatant liquid was yellow, red, greenish-brown or blood red depending on whether the metal was zinc, copper, cobalt or nickel	15
8.	Zinc thiocarbonate ($ZnCS_3$)	Cream	$Zn(NO_3)_2$	0.1 M		
9.	Iron thiocarbonate ($FeCS_3$)	Brownish-black	$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	0.2 M	Obtained by adding PTC to metal tartrate complex in ammoniacal medium	15
10.	Silver sulphide (Ag_2S)	Black	$AgNO_3$	0.1 M	Precipitated from ammoniacal medium and digested on steam bath for half an hour	
11.	Copper sulphide (CuS)	Black	$CuSO_4 \cdot 5H_2O$	0.2 M	Obtained from solns. which were made acidic with 4N HCl (pH 0.7-1.0; green spot on methyl violet	15, 16

12.	Cadmium sulphide (CdS)	Yellow	$\text{Cd}(\text{NO}_3)_2$	0.2 M	paper), by adding PTC for complete precipitation and digesting on steam bath for half an hour	15
13.	Mercury sulphide (HgS)	Black	HgCl_2	0.2 M		
14.	Bismuth sulphide (Bi_2S_3)	Black	BiONO_3	0.2 M		
15.	Molybdenum sulphide (MoS_2)	Black	$(\text{NH}_4)_2\text{MoO}_4 \cdot 12\text{H}_2\text{O}$	0.5 M		
16.	Platinum sulphide (PtS_2)	Brownish-black	H_2PtCl_6	0.1 M	PTC added dropwise to acid soln. (1.5–2N) with respect to H_2SO_4 with constant stirring. The final acidity was adjusted to 1 M and solution digested over a steam bath for about an hour Precipitated by adding PTC to hot (95°C) acid soln. (2–3 ml 12N HCl for every 100 ml) till the precipitation was complete	16
17.	Gold sulphide (Au_2S_3)	Brown-black	HAuCl_4	0.1 M		
18.	Vanadium sulphide (V_2S_5)	Dark brownish-black	NH_4VO_3	0.5 M	PTC added to obtain soluble thiocarbonate-complex; subsequent acidification with 1.5–2N HCl followed by digestion on steam bath for about half an hour	13, 16
19.	Selenium sulphide (SeS_2)	Lemon yellow	Na_2SeO_3	0.5 M		
20.	Tellurium sulphide (TeS_2)	Dark brown	K_2TeO_3	0.5 M		
21.	Arsenic sulphide (As_2S_3 or As_2S_5)	Yellow	NaAsO_2 , NaAsO_3	0.2 M	Precipitated by adding PTC to hot acid solution (1N with respect to HCl) and digesting for half an hour	15, 16, 23
22.	Antimony sulphide (Sb_2S_3)	Orange	Potassium antimony tartrate	0.2 M		

In all cases the precipitate was collected by filtration through Whatman filter paper No. 42, washed thoroughly with water and then with 8% alcohol. Drying of the precipitate was done at room temperature for about 72 hours by keeping in a vacuum desiccator.

(iii) difference in the thermolysis of metal sulphides resulting from the use of PTC as against those products which are obtained with such sulphide precipitants as hydrogen sulphide, sodium sulphide, thioacetamide or thiosulphate.

Furthermore, TG of copper sulphide and cadmium sulphide precipitated directly with PTC has been carried out in order to compare their modes of transformation with those of the products resulting from thermolysis of copper thiocarbonate and cadmium thiocarbonate precipitated initially from alkaline medium with PTC.

Experimental

Potassium thiocarbonate (PTC) reagent. An aqueous solution of PTC (1 M) prepared by the modified direct method [20] was used as a stock solution and its working solutions were obtained by suitable dilutions.

Reagents and metal ion solutions. Prepared by dissolving analytical grade salts (B. D. H., Analar or Merck, G. R.) in distilled water. All other chemicals used were of analytical grade.

Thermorecording balance used. The thermogravimetric data were collected using a Stanton's thermorecording balance model TR-1, installed at the Central Road Research Institute, New Delhi.

The preparatory methods of metal thiocarbonates and sulphides are summarized in Table 1.

Thermogravimetric behaviour

Thermogravimetric procedure. A weighed sample of dried metal thiocarbonate/sulphide (250–1000 mg) was transferred to a crucible freshly tared after heating to 1000° and subsequently stored in a desiccator. The sample was subjected to a heating rate of $4 \pm 0.2^\circ$ per minute in an atmosphere of air. The data were collected for a range of temperatures up to 1000°. The period of maximum rise in temperature was about 4 hrs. The sensitivity of the balance per small chart division was 1 mg and the chart range was 100 mg. All data used in the preparation of the thermogravimetric curves were corrected for buoyancy (experimentally determined for the crucible used). The TG curves shown were obtained by plotting different points of the original graph on X and Y axes.

Potassium thiocarbonate (K_2CS_3). An initial loss of adherent water up to 120° was recorded as shown by the TG curve (Fig. 1). Further decrease in weight from 120° to 350° was due to the loss of carbon disulphide from K_2CS_3 . This loss in weight was first abrupt and subsequently gradual, and during this interval K_2CS_3 was converted into K_2S . Simultaneous partial oxidation of potassium sulphide gave a visible minimum at 350° due to the mixed character of the product at this stage. From 350° to 550° there was an increase in weight apparently due to the

progressive oxidation of K_2S to potassium persulphate ($K_2S_2O_8$). The persulphate further decomposed into potassium sulphate and the decomposition was complete by 760° . The constant weight of the residual product between 760° and 1000° corresponded to the composition K_2SO_4 .

Thalious thiocarbonate (Tl_2CS_3). Thalious thiocarbonate was found to be thermally stable up to 130° , as seen from the thermogram (Fig. 1). Between 130° and 180° , the product apparently lost carbon disulphide yielding thallium sulphide which was simultaneously partially oxidized. A visible minimum at 180° was obtained because of the mixed product affecting the normal course of the curve.

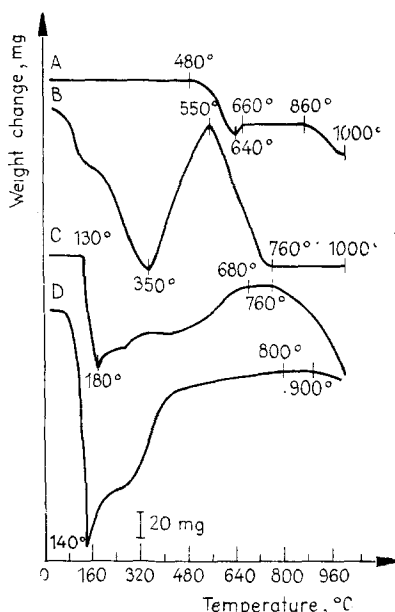


Fig. 1. TG curves of A: silver sulphide (Ag_2S), B: potassium thiocarbonate (K_2CS_3), C: thalious thiocarbonate (Tl_2CS_3) D: lead thiocarbonate ($PbCS_3$)

Over the broad temperature range of 180° to 680° , there was a continuous increase in weight showing progressive oxidation of thalious sulphide to thalious sulphate. The horizontal level between 680° and 760° corresponded to the expected weight of Tl_2SO_4 . Beyond 760° , there was a continuous loss in weight due to the decomposition of the sulphate to oxide. Further loss in weight resulted from the eventual sublimation of the oxide. Similar loss has also been reported by Duval [17] in connection with the thermolysis of pure thalious sulphate.

Lead thiocarbonate ($PbCS_3$). The TG curve as illustrated in Fig. 1 showed an initial loss in weight of the sample of $PbCS_3$ up to 140° . This loss was apparently due to the loss of carbon disulphide and some adherent moisture. The presence of moisture was confirmed from the final weight of the product. PbS result-

ing therefrom underwent partial oxidation to sulphate and gave a visible minimum at 140° . Above 140° , there was a progressive increase in weight up to 480° . Thereafter, the gain was not appreciable, although complete oxidation of PbS to PbSO_4 was achieved by 800° . The horizontal portion of the curve between 800° and 900° corresponded to the composition PbSO_4 equivalent to the initial weight of the test sample of lead thiocarbonate. This tallied with the observations made by Duval [17] regarding the thermolysis of PbS and PbSO_4 . The resulting amount of PbSO_4 showed that the test sample of PbCS_3 contained about 1.2 per cent adherent moisture. Above 900° , the PbSO_4 started to decompose. Terem and Aklam [24] reported 860° as the decomposition temperature for pure PbSO_4 .

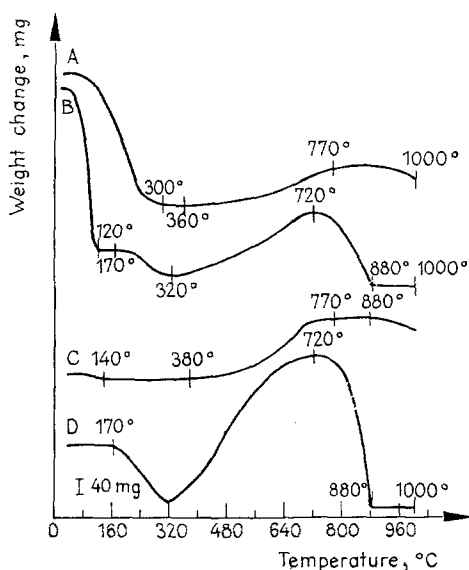


Fig. 2. TG curves of A: cadmium thiocarbonate (CdCS_3), B: copper thiocarbonate (CuCS_3), C: cadmium sulphide (CdS), D: copper sulphide (CuS)

Silver sulphide (Ag_2S). A critical review of the thermal behaviour of silver sulphide precipitated by different thioreagents has been given by Duval [17]. According to Taimni and Tandon [25] silver sulphide precipitated by sodium sulphide gave almost a horizontal line extending up to 570° . Silver sulphide obtained with hydrogen sulphide showed a horizontal line extending from 69 to 615° . Ishii [26] recommended hot air drying of the sulphide above 170° . Ag_2S obtained with sodium thiosulphate by Faktor [17] was completely dry near 120° and remained stable up to 649° .

The TG curve of silver sulphide precipitated with PTC is given in Fig. 1. The sample of silver sulphide yielded a horizontal line extending up to 480° and the weight at this stage corresponded to the sulphide form. Its decomposition started at 480° giving a visible minimum at 640° . Slight increase in weight was recorded

up to 660° due to the mixed product, with a horizontal line up to 860° , the mixture contained metallic silver and silver sulphate in indefinite proportion. Beyond 860° , there was a continuous loss in weight due to the decomposition of the sulphate into metal; the conversion into metal was complete by 980° . Thus for the gravimetric estimation of silver as Ag_2S the product can be safely heated up to 480° and weighed.

Copper thiocarbonate (CuCS_3). A sample of copper thiocarbonate on thermolysis initially showed a loss of carbon disulphide and moisture up to 120° (Fig. 2). The product, which remained unchanged between 120° and 170° , corresponded to the composition of cupric sulphide. Between 170° and 320° there was further loss in weight apparently due to the removal of combined sulphur from cupric sulphide and its consequent conversion into cuprous sulphide. Cu_2S was partially oxidized and gave a visible minimum at 320° due to the mixed character of the product at this stage. A subsequent increase in weight was recorded up to 720° due to the oxidation of Cu_2S to CuO/CuSO_4 . From 750° to 880° , decomposition of CuSO_4 into its oxide occurred. The weight of the product, which remained constant from 880° to 1000° , corresponded to the composition of CuO . The recorded weight of CuO showed that the test sample of CuCS_3 contained nearly 1.9 per cent of adherent moisture. The mode of decomposition of CuCS_3 after the sulphide stage was further confirmed from the thermolysis of CuS initially precipitated with PTC and studied separately as described in the following.

Copper sulphide (CuS). Duval [17] has already reported the thermolysis of cupric sulphide precipitated with hydrogen sulphide, thioacetic acid, thioacetamide and thiosulphate. The present studies relate to cupric sulphide precipitated with PTC. The thermogram of cupric sulphide precipitated with PTC is shown in Fig. 2. It may be noticed that there was no appreciable loss in weight of the precipitate up to 170° . Above 170° the product started losing combined sulphur till it was gradually converted into cuprous sulphide. The cuprous sulphide after having been partially oxidized gave a minimum at 320° . The progressive increase in weight from 320° to 720° was apparently due to the oxidation of cuprous sulphide into a mixture of CuO and anhydrous CuSO_4 . Above 720° decomposition of the sulphate started and was complete by 880° , yielding the oxide. Ishii [26] prescribed a temperature of at least 850° for the complete conversion of cupric sulphide into cupric oxide. The weight of the product remained unchanged between 880° and 1000° , corresponding to the composition CuO . The thermolysis curve of cupric sulphide precipitated with PTC resembles closely that of cupric sulphide precipitated with other sulphide precipitants.

Cadmium thiocarbonate (CdCS_3). A sample of CdCS_3 lost moisture and carbon disulphide up to 300° . The weight of the product remained constant till 360° (Fig. 2). The horizontal line between 300° and 360° almost corresponded to the weight of CdS . From 360° to 770° , there was an increase in weight apparently due to the oxidation of CdS to CdSO_4 . The oxidation was not quantitative as part of the CdS sublimed above 770° . Consequently, the level in the curve which extended from 770° to 850° did not correspond to the composition CdSO_4 , but

the recorded weight was much less than the required weight of CdSO_4 obtainable from the test sample of CdCS_3 initially taken. Above 850° , CdSO_4 started losing weight apparently due to its decomposition into CdO or due to its volatilization at elevated temperature. Ostroff and Sanderson [27] have already reported that pure anhydrous CdSO_4 starts decomposing at 816° , while Duval [17] reported that a sample of CdS when subjected to thermal analysis at about 1000° resulted in a mixture of CdO , CdS and CdSO_4 .

Cadmium sulphide (CdS). Thermolysis of CdS precipitated with hydrogen sulphide, sodium sulphide or thiosulphate has been reviewed by Duval [17]. A sample

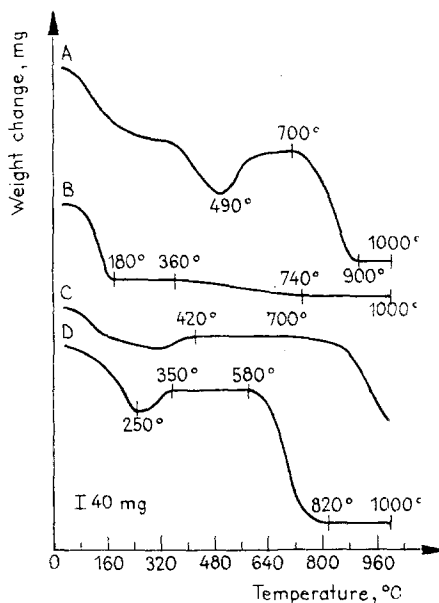


Fig. 3. TG curves of A: nickel thiocarbonate (NiCS_3), B: zinc thiocarbonate (ZnCS_3), C: cobalt thiocarbonate (CoCS_3), D: iron thiocarbonate (FeCS_3)

of CdS precipitated with PTC remained almost stable from 140° to 380° (Fig 2). The initial loss in weight up to 140° was apparently due to the escape of adherent water (12 mg) present in the test sample. There was a progressive increase in the weight of the product from 380° to 770° showing CdS to have undergone partial oxidation to CdSO_4 followed by partial sublimation. This was indicated by the horizontal portion of the curve which extended from 770° to 880° . But the weight did not correspond to the composition CdSO_4 equivalent to the weight of CdS started with. Above 880° a loss in weight was recorded due to the decomposition of CdSO_4 to CdO and subsequently, the oxide having undergone volatilization. These results are nearly in agreement with the observations made by Ostroff and Sanderson [27] and also by Duval regarding the decomposition of CdSO_4 and CdS

(precipitated by other sulphide precipitants) studied by them separately. Taimni and Salaria [28], however, first reported that cadmium sulphide precipitated by sodium sulphide lost weight up to 140°, but later on Taimni and Tandon [25] found that the weight remained constant up to 300°.

Iron thiocarbonate (FeCS₃). The sample of FeCS₃ on thermolysis (Fig. 3) showed an initial loss of weight up to 250°, apparently due to the removal of adherent or adsorbed water and carbon disulphide. Absence of any horizontal portion before 250° showed that at no stage was FeS stable. At 250°, FeS which was partially oxidized gave a visible minimum because of the mixed nature of the product at this stage. From 250° to 350°, there was a sudden increase in weight showing complete conversion of FeS into FeSO₄. There was only slight increase in the weight of the product between 350° and 580°. But the weight of the product at the maximum (580°) did not correspond to the required weight of the sulphate. It was less, apparently due to a mixed product containing sulphate and oxide. The sulphate increasingly began to decompose around 600°, and beyond 820° only Fe₂O₃ remained. The final weight of Fe₂O₃ showed that the test sample of FeCS₃ contained about 1 per cent of moisture. Duval [17] has also reported that a sample of ferrous sulphide was converted to Fe₂O₃ from 800° onwards.

Cobalt thiocarbonate (CoCS₃). Fig. 3 represents the TG curve of a sample of cobalt thiocarbonate. The sample of CoCS₃ lost weight up to 320° apparently due to the loss of carbon disulphide, and was converted into CoS. As CoS was formed, it gradually became oxidized to sulphate and the partially oxidized CoS gave a visible minimum at 320° due to the mixed nature of the product at this stage. Above 320° there was an increase in the weight of the product due to the oxidation of CoS to CoSO₄. The complete oxidation was marked by a horizontal level of the curve extending from 420° to 710° and corresponded to the composition CoSO₄. According to Duval [17] there is no agreement as to the highest temperature at which anhydrous cobalt sulphate can exist, and temperatures have been reported ranging from 550° to 880°. Above 710°, the product started losing weight due to the decomposition of CoSO₄. The decomposition temperature of CoSO₄ almost tallies with the decomposition temperature of 708° reported for pure CoSO₄ by Ostroff and Sanderson [27].

Nickel thiocarbonate (NiCS₃). A sample of nickel thiocarbonate showed an initial loss in weight up to 490°, apparently due to the removal of carbon disulphide and adherent water, resulting in the formation of nickel sulphide (Fig. 3). A visible minimum was recorded at 490° due to the partially oxidized nickel sulphide. Between 490° and 700° the increase in weight was due to the oxidation of the NiS to NiSO₄. However, the gain in weight between 600° and 700° was only slight. The product then lost weight up to 900° and was converted into oxide. The horizontal line from 900° onwards almost corresponded to the composition NiO. The weight of the oxide from the curve showed that the test sample of nickel thiocarbonate contained about 2 per cent adherent water. Demassieux and Mallard [29] studied the thermolysis of pure nickel sulphate and found that it yielded NiO on heating beyond 880°.

Zinc thiocarbonate ($ZnCS_3$). The sample of $ZnCS_3$ on thermolysis (Fig. 3) showed an initial loss in weight up to 180° , apparently due to the removal of adherent or adsorbed water and carbon disulphide. Beyond 180° the curve remained horizontal up to 360° and corresponded to ZnS . Thereafter, the loss in weight was very small till 480° when a sudden decrease in weight showed conversion into oxide which was complete by 740° . The horizontal level between 740° and $1000^\circ C$ corresponded to the composition ZnO . The thermolysis curve reveals that no $ZnSO_4$ was formed at any stage and this tallies with the information reported by Duval [17] as well. However, some workers [30] have reported the formation of sulphate. For the estimation of zinc, the suitable weighing form is ZnS heated over the temperature range $180\text{--}360^\circ$, or ZnO when heated above 740° .

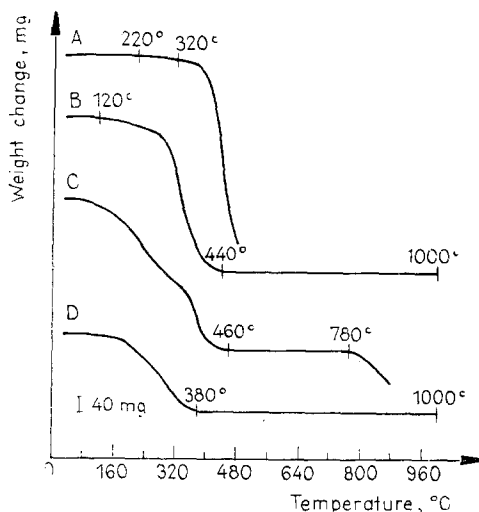


Fig. 4. TG curves of A: mercury sulphide (HgS), B: platinum sulphide (PtS_2), C: molybdenum sulphide ($MoS_3 \cdot 2H_2O$), D: gold sulphide (Au_2S_3)

Molybdenum(VI) sulphide ($MoS_3 \cdot 2H_2O$). The thermal behaviour of molybdenum(VI) sulphide precipitated with hydrogen sulphide and sodium sulphide was studied by Moser and Beer [31] and by Taimni and Tandon [32], respectively. Herstein [33] studied molybdenum sulphide precipitated by thioacetic acid. A critical review of the thermal behaviour of molybdenum sulphide precipitated by different thio-reagents has been given by Duval [17] as well. The present thermolysis studies of molybdenum sulphide precipitated with PTC agreed quite closely with that of the sample precipitated with hydrogen sulphide and studied by Moser and Beer [31].

The TG curve of molybdenum sulphide precipitated with PTC is given in Fig. 4. The precipitate lost weight continuously up to 460° due to the gradual loss of

water and sulphur from the product. The resultant product remained unchanged from 460° onwards and followed a horizontal course which extended as far as 780°. The weight of this product between 460° and 780° corresponded to the composition MoO_3 . From 780° onwards there was a decrease in weight due to volatilization of the oxide, which according to Taimni and Tandon [32] volatilizes at about 800°. The final weight of the oxide as indicated by the curve showed that in addition to two moles of water per mole of the sample, there was adherent or adsorbed water present to the extent of 1.7 per cent in the test sample. Thus, for the gravimetric estimation of molybdenum as MoO_3 , the sulphide precipitate may be ignited between 500° to 750° to obtain the oxide.

Platinum(IV) sulphide (PtS_2). Platinum(IV) sulphide was found to be thermally stable up to 120° as seen from the thermogram (Fig. 4). Beyond 120°, the thermolysis curve slanted continuously downwards until the temperature reached 440°, thereafter remaining horizontal up to 1000° due to the formation of platinum metal. However, the weight of the metal did not correspond to the initial composition PtS_2 , presumably due to the initial product containing some elemental sulphur.

Duval [17] studied the thermolysis of platinum sulphide precipitated with hydrogen sulphide but was unable to find any horizontal level corresponding to a sulphide of definite composition. Taimni and Tandon [25] carried out the thermolysis of PtS_2 precipitated with sodium sulphide, and they too were unable to find any horizontal level relating to a definite sulphide. It was beyond 440° that the plot showed a persistent horizontal section corresponding to platinum metal.

Gold sulphide (Au_2S_3). The thermolysis curve (Fig. 4) showed an initial loss in weight which was apparently caused by the removal of adherent water. The subsequent rapid loss was due to the removal of sulphur. The sulphide did not yield any horizontal line; the horizontal line beyond 380° corresponded to the metal.

According to Ishii [26] the sulphide yielded gold above 350°. However, according to Taimni and Tandon [32], the sulphide obtained with sodium sulphide gave a horizontal line up to 220° after which it decomposed to the metal completely by 280°.

This has revealed that the sulphide precipitated with PTC was contaminated with elemental sulphur and hence did not correspond to any definite composition. Consequently, the ignition of the sulphide above 380° is necessary for the gravimetric estimation of gold after its precipitation as sulphide.

Mercuric sulphide (HgS). The sample of mercuric sulphide gave a horizontal line up to 220° showing the stability of the sulphide up to 220°; beyond this it started decomposing slowly till 320°, and then abruptly around 400°. The crucible was completely empty by the time the temperature had reached 490° (Fig. 4).

Taimni and Tandon [32] studied the thermal behaviour of mercuric sulphide obtained with sodium sulphide. According to them the product showed a horizontal line as far as 300°, after which decomposition started and the crucible was empty by 500°. A critical review of the thermal behaviour of samples of mercuric sulphide obtained with different thio-reagents has been given by Duval [17]. The

present study of the product obtained with PTC have determined the optimum temperature as 220° for obtaining the weighing form of mercury as sulphide.

Vanadium(V) sulphide (V_2S_5). The TG curve of vanadium(V) sulphide (Fig. 5) showed an initial loss of weight apparently due to the loss of water and sulphur retained by the precipitated product. The resultant oxide, V_2O_5 , remained unchanged from 300° onwards and followed a horizontal course which extended as far as 1000° .

As vanadium pentasulphide did not produce any horizontal level, the sulphide weighing form of vanadium cannot yield accurate results. Separation of vanadium(V) as pentasulphide being possible with PTC, its gravimetric estimation as oxide, V_2O_5 , after igniting the sulphide above 300° would be accurate. The temperature range for the constancy in weight of the oxide is $300\text{--}1000^\circ$.

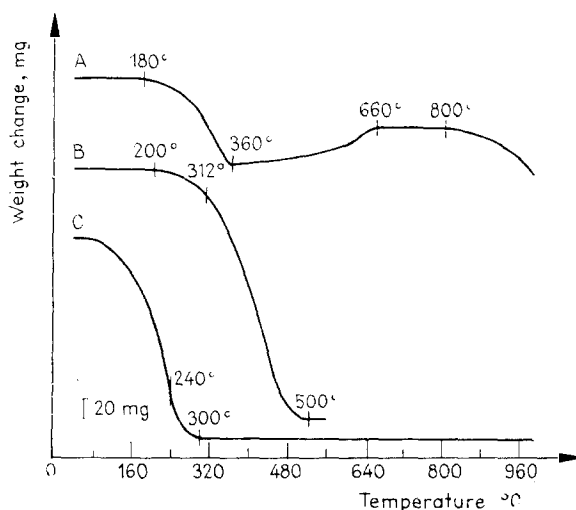


Fig. 5. TG curves of A: tellurium sulphide (TeS_2), B: selenium sulphide (SeS_2), C: vanadium sulphide (V_2S_5)

Selenium(IV) sulphide (SeS_2). The thermal behaviour of selenium(IV) sulphide precipitated with sodium sulphide has been studied by Taimni and Tandon [25] who reported that it was stable up to 210° beyond which it began to sublime.

The thermolysis studies of selenium sulphide obtained with PTC showed a trend in weight change similar to that of the product obtained with sodium sulphide by Taimni and Tandon [25]. As shown by the thermogram (Fig. 5), the disulphide remained stable up to 200° , after which there was a loss in weight. The loss was slow in the temperature range $200^\circ\text{--}312^\circ$, then became rapid, and loss was complete at 500° . The initial slow loss in weight was found to be due to the oxidation of the disulphide to the dioxide, SeO_2 . The oxide started subliming at 312° and its sublimation was complete by 500° ; this is also confirmed from the

literature [34]. Selenium sulphide precipitated with PTC, after drying up to 200°, can be weighed for its estimation.

Tellurium(IV) sulphide (TeS_2). Tellurium(IV) sulphide remained stable up to 180° as seen from the TG curve (Fig. 5). Beyond 180° it began to decompose and the decomposition, apparently to tellurium, continued up to 360°. There was a slight increase in weight from 360° to 420°, presumably due to the start of oxidation of the sulphide. Beyond 420°, the weight progressively increased and this continued up to 660°. The weight between 660—800° remained constant and corresponded to the required weight of TeO_2 ; this began subliming after 800°. According to Taimni and Tandon [25], tellurium sulphide precipitated with sodium sulphide showed almost a similar trend in weight change with rise in temperature.

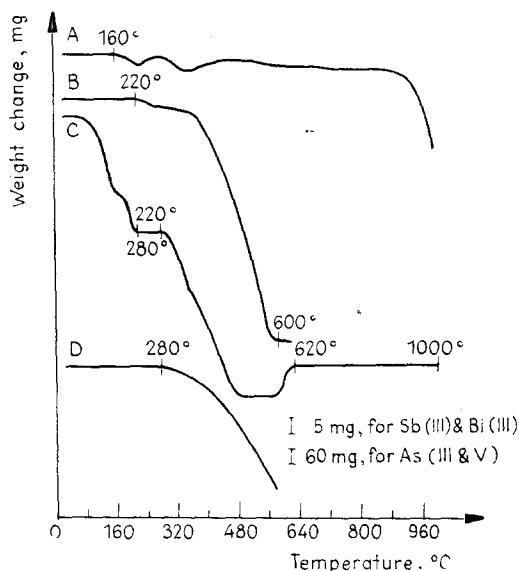


Fig. 6. TG curves of A: bismuth sulphide (Bi_2S_3), B: arsenic(III) sulphide (As_2S_3), C: antimony sulphide (Sb_2S_3) D: arsenic(V) sulphide (As_2S_5)

Tellurium can be separated as a stable sulphide with PTC and estimated as disulphide after drying up to 180°. But, due to the wide horizontal level between 660° and 800°, estimation of tellurium as dioxide would be preferable after its separation as sulphide with PTC.

Arsenic trisulphide (As_2S_3). A sample of arsenic trisulphide gave a horizontal level up to 220° showing the stability of the sulphide up to 220°. Beyond this temperature, it sublimed and was superficially oxidized. The crucible was completely empty by the time the temperature had reached 600° (Fig. 6) except for a trace of residue which did not change in weight.

The observations tally with the TG studies of As_2S_3 precipitated with hydrogen sulphide, as carried out by Duval [17], thus establishing the purity of As_2S_3 precipitated with PTC.

Arsenic pentasulphide (As_2S_5). The sample of arsenic pentasulphide gave a horizontal level up to 280° , showing the absence of free sulphur and stability of the sulphide up to 280° . Beyond this temperature it sublimed and was superficially oxidized. The crucible was completely empty by the time the temperature had reached 580° (Fig. 6). Taimni and Tandon [32] reported that As_2S_5 precipitated with sodium sulphide remained stable up to 270° , and the crucible was empty by the time the temperature had reached 550° .

Duval [17], who studied the thermal behaviour of a sample of As_2S_5 precipitated by hydrogen sulphide, found that it yields a horizontal line extending from 78° to 245° and that the sulphide sublimed beyond this temperature. Yosida [35] reported that a precipitate of As_2S_5 decomposed when dried above 130° . Presumably, it was due to the presence of free sulphur in the product studied by him. The initial loss in weight before 78° , as indicated by Duval [17], might have been due to the presence of some adherent water.

Antimony trisulphide (Sb_2S_3). Duval [17] studied the thermal behaviour of antimony trisulphide precipitated with hydrogen sulphide. Taimni and Tandon [32] studied a sample precipitated with sodium sulphide. The thermogram of antimony trisulphide precipitated with PTC is as shown in Fig. 6. It recorded an initial loss in weight up to 220° , apparently due to the removal of sulphur and moisture. The horizontal line between 220° and 280° corresponded to the pure sulphide. Beyond 280° , the sulphide was oxidized to Sb_2O_3 ; the latter, on combining more oxygen, gave yet another horizontal line from 480° to 570° due to a mixed product containing the higher oxide, Sb_2O_4 . The oxidation of Sb_2O_3 to Sb_2O_4 was complete by 620° . The third horizontal line, extending from 620° to 1000° , corresponded to the composition Sb_2O_4 .

Bismuth sulphide (Bi_2S_3). Bismuth trisulphide gave a horizontal line up to 160° (Fig. 6) showing its stability. Beyond 160° no other horizontal line corresponded to any definite composition. The residue at 1000° was light yellow possibly due to the mixture of bismuth sulphate and oxide.

Duval [17], who studied the thermal behaviour of a sample of Bi_2S_3 precipitated with hydrogen sulphide, reported an extremely capricious curve. The slightly ascending level between 100° and 165° corresponded to the probable region of the sulphide. Bismuth sulphide obtained with sodium thiosulphate [36] did not provide any horizontal line. Taimni and Tandon [25] obtained bismuth sulphide with sodium sulphide; this yielded a horizontal line up to 160° , as confirmed by the present investigations of the sulphide obtained with PTC.

*

We wish to express our thanks to Emeritus Prof. T.R. Seshadri, F.R.S., for his keen interest in the work. We are also grateful to Prof. R. P. Mitra, F. N. I., Head of the Chemistry Department, University of Delhi, for providing us with necessary facilities, and to the Director, Central Road Research Institute, New Delhi, for providing the use of the thermobalance at

the Institute. Finally, the authors acknowledge with thanks the financial assistance from the Council of Scientific and Industrial Research, Govt. of India, which sponsored the research scheme under which the present work was carried out.

References

1. K. N. JOHRI, *J. Sci. Industr. Res.*, 17B (1958) 333.
2. K. N. JOHRI, *J. Sci. Industr. Res.*, 18B (1959) 430.
3. K. N. JOHRI, *Ind. J. Appl. Chem.*, 28 (1963) 114.
4. K. N. JOHRI, Macro and semimicro chemical analysis without H₂S using potassium tri-thiocarbonate. Asia Publishing House, Bombay-1, 2nd Ed., 1968.
5. K. N. JOHRI and K. SINGH, *Curr. Sci.*, 34 (1965) 78.
6. K. N. JOHRI and K. SINGH, *Curr. Sci.*, 34 (1965) 582.
7. K. N. JOHRI, N. K. KAUSHIK and K. SINGH, *Mikrochim. Acta*, (1969) 737.
8. K. N. JOHRI and K. SINGH, *Curr. Sci.*, 34 (1965) 661.
9. K. N. JOHRI and K. SINGH, *J. Appl. Chem.*, 28 (1965) 90.
10. K. N. JOHRI and K. SINGH, *Bull. Chem. Soc. (Japan)*, 40 (1967) 990.
11. K. N. JOHRI and K. SINGH, *Indian J. Appl. Chem.*, 30 (1967) 1.
12. K. N. JOHRI and K. SINGH, *Indian J. Appl. Chem.*, 31 (1968) 94.
13. K. N. JOHRI, N. K. KAUSHIK and K. SINGH, *Talanta*, 16 (1969) 432.
14. K. N. JOHRI and K. SINGH, *Mikrochim. Acta*, (1969).
15. K. SINGH, Ph.D. Thesis, University of Delhi, 1967.
16. N. K. KAUSHIK, Ph.D. Thesis, University of Delhi, 1969.
17. CL. DUVAL, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam, 1963.
18. K. N. JOHRI, N. K. KAUSHIK and K. SINGH, *Curr. Sci.*, 36 (1967) 458.
19. K. N. JOHRI, N. K. KAUSHIK and K. SINGH, *Curr. Sci.*, 36 (1967) 515.
20. K. N. JOHRI and K. SINGH, *Indian J. Chem.*, 3 (1965) 158.
21. J. W. MELLOR, *A. Comprehensive Treatise on Inorganic and Theoretical Chemistry*. Longmans, Green & Co., London, 1961, Vol. VI, pp. 119—129.
22. L. GORDON, M. L. SALUTSKY and H. H. WILLARD, *Precipitation from Homogeneous Solution*. John Wiley & Sons, Inc., New York, 1959.
23. K. N. JOHRI, N. K. KAUSHIK and K. SINGH, *Curr. Sci.*, 37 (1968) 699.
24. H. N. TEREM and S. AKLAM, *Compt. rend.*, 232 (1951) 973.
25. I. K. TAIMNI and S. N. TANDON, *Anal. Chim. Acta*, 22 (1960) 553.
26. K. ISHII, *J. Chem. Soc. (Japan)*, 52 (1931) 167.
27. A. G. OSTROFF and R. T. SANDERSON, *J. Inorg. Nuclear Chem.*, 9 (1959) 45.
28. I. K. TAIMNI and G. B. S. SALARIA, *Anal. Chim. Acta*, 11 (1954) 54.
29. DEMASSIEUX and MALARD, *Compt. rend.*, 245 (1957) 1544.
30. L. ERDEY, *Gravimetric Analysis, Part II*. Pergamon Press, Oxford, 1965, p. 424.
31. L. MOSER and M. BEER, *Z. anorg. Chem.*, 134 (1924) 67.
32. I. K. TAIMNI and S. N. TANDON, *Anal. Chim. Acta*, 22 (1960) 34.
33. B. HERSTEIN, *U. S. Dept. Agr. Bull.*, No. 150, p. 44. C. A., 1913, 37.
34. *Handbook of Chemistry and Physics*. Chemical Rubber Pub. Co., U.S.A., 44th Ed., 1963, p. 644.
35. Y. YOSIDA, *J. Chem. Soc. (Japan)*, 60 (1939) 915.
36. F. FAKTOR, *Pharm. Post*, 33 (1900) 301, 317.

RÉSUMÉ — On a étudié le comportement thermogravimétrique des thiocarbonates de K(I), Ti(I), Pb(II), Cd(II), Cu(II), Co(II), Ni(II), Zn(II), Fe(II) et des sulfures de Ag(I), Cu(II), Cd(II), Hg(II), Bi(III), Mo(VI), Pt(IV), Au(III), V(V), Se(IV), Te(IV), As(III, V) et Sb(III). Par précipitation en milieu homogène on produit des précipités de thiocarbonates purs. On a déterminé les valeurs de température entre lesquelles les précipités sont constants en poids. Possibilité au dosage gravimétrique des métaux présents en quantités de milligrammes.

ZUSAMMENFASSUNG — Es wurde das Verhalten der Thiokarbonate von K(I), Tl(I), Pb(II), Cd(II), Cu(II), Co(II), Ni(II), Zn(II), Fe(II) und der Sulphide von Ag(I), Cu(II), Cd(II), Hg(II), Bi(III), Mo(VI), Pt(IV), Au(III), V(V), Se(IV), Te(IV), As(III, V) und Sb(III) thermogravimetrisch untersucht. Die durch homogene Fällung erhaltenen Thiokarbonatniederschläge waren entsprechend rein. Es wurden die Temperaturgrenzen der Gewichtskonstanz der Niederschläge zum Zwecke der gravimetrischen Bestimmung von Metallen in Milligrammengen festgestellt.

Резюме — С помощью термического анализа исследованы тиокарбонаты K(I), Tl(I), Pb(II), Cd(II), Cu(II), Co(II), Ni(II), Zn(II), Fe(II), и сульфиды, Ag(I), Cu(II), Cd(II), Hg(II), Bi(III), Mo(VI), Pt(IV), Au(III), V(V), Se(IV), Te(IV), As(III, V), Sb(III). Эти исследования не только показали чистоту осажденных продуктов, полученных с тиокарбонатом калия (ПТС), но и определили правильную температурную область при осаждении для достижения постоянного веса, что дает возможность гравиметрической пренки точного количества [мг] исследуемых ионов металлов. Чистота осажденных продуктов достигалась путем осаждения из гомогенного раствора, при использовании ПТС-реагента в качестве осаждающего вещества.