

## Electrometric Investigations on the Acid-Orthothioantimonite System and the Formation of Heavy Metal Thioantimonites

Shiva Prasad

Departamento de Engenharia Química, Centro de Ciências e Tecnologia,  
Universidade Federal da Paraíba, Campina Grande - PB, Brazil

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A estequiometria dos ânions formados durante a reação entre ácidos (HCl, CH<sub>3</sub>COOH) e orto-tioantimonito de sódio foi investigado por meio de técnicas eletrométricas envolvendo as titulações de pH e condutométricas, bem como pelo método de Job de variação contínua. Os degraus e inflexões nas curvas de titulação e os máximos das curvas de variação contínua fornecem evidências incontestáveis da existência de três diferentes espécies aniônicas, a saber, SbS<sub>3</sub><sup>3-</sup>, Sb<sub>2</sub>S<sub>5</sub><sup>4-</sup> e SbS<sub>2</sub><sup>-</sup> nas faixas de pH (>11,5), (8,7-9,1) e (6,6-7,1), respectivamente. Foi observado que uma adição em excesso dos ácidos os ânions tioantimonitos finalmente são convertidos em trissulfeto de antimônio. As titulações de pH e condutométricas entre Th<sup>4+</sup> e os ânions tioantimonitos (SbS<sub>3</sub><sup>3-</sup>, Sb<sub>2</sub>S<sub>5</sub><sup>4-</sup> e SbS<sub>2</sub><sup>-</sup>) indicaram a formação de ortho-3ThS<sub>2</sub>.2Sb<sub>2</sub>S<sub>3</sub> e piro-ThS<sub>2</sub>.Sb<sub>2</sub>S<sub>3</sub> tioantimonitos de tório nas vizinhanças de pH 6,1 e 5,2, respectivamente.

The stoichiometry of the anions formed during the reaction between acids (HCl, CH<sub>3</sub>COOH) and sodium ortho-thioantimonite was investigated by means of electrometric techniques involving pH and conductometric titrations, as well as by Job's method of continuous variation. The breaks and inflections in the titration curves and maxima from the continuous variation study provide definite evidence for the existence of three different anionic species, viz. SbS<sub>3</sub><sup>3-</sup>, Sb<sub>2</sub>S<sub>5</sub><sup>4-</sup> and SbS<sub>2</sub><sup>-</sup> in the pH ranges (>11.5), (8.7-9.1) and (6.6-7.1), respectively. Upon the addition of an excess of the acids the thioantimonite anions ultimately convert into antimony trisulfide. The pH and conductometric titrations between Th<sup>4+</sup> and the thioantimonite anions (SbS<sub>3</sub><sup>3-</sup>, Sb<sub>2</sub>S<sub>5</sub><sup>4-</sup> and SbS<sub>2</sub><sup>-</sup>) indicated the formation of thorium ortho-3ThS<sub>2</sub>.2Sb<sub>2</sub>S<sub>3</sub> and pyro-ThS<sub>2</sub>.Sb<sub>2</sub>S<sub>3</sub> thioantimonite in the vicinity of pH 6.1 and 5.2 respectively. Analytical investigations confirmed the results obtained by the electrometric study.

**Keywords:** thioantimonite, thorium thioantimonites, electrometric study

### Introduction

Antimony is not used in industry in the unalloyed state to any extent. Its main use in the metallic state is as a constituent of many alloys, to which it imparts certain desired properties, such as expansion on solidification, increased hardness, and corrosion resistance<sup>1</sup>. The electrodeposition of antimony alloys employ antimonites and thioantimonites in alkaline media<sup>2,3</sup>. The electrodeposits of antimony alloys are generally brittle and stressed and do not adhere well to the base metal. So far, the baths developed have very few practical applications. The properties of antimony and its low cost could make electrodeposited antimony very useful if a really satisfactory plating bath were developed.

The problem in the electrodeposition bath seems to be due to the complicated aqueous solution chemistry of antimony. The anionic species of antimony change with the pH of the bath. It has been reported<sup>4</sup> that investigations on antimony are made difficult by the fact that it sometimes appears as Sb(III) and Sb(V) in the same compound. The antimony compounds are formally similar, but because of the tendency of antimony to form five or six bonds, the species in aqueous solution of similar arsenic and antimony compounds may be different.

With the intention of studying in detail the chemistry of the decomposition of alkaline ortho-thioantimonite upon acidification, establishing the stoichiometry of intermediate species, and examining the suitable conditions for their stability and existence it was considered worthwhile to make a careful and precise study of the acid-thioantimonite

system by electrometric techniques, which have provided more conclusive evidence of the condensation processes of thioanions of tungsten<sup>5</sup>, molybdenum<sup>6</sup> and arsenic<sup>7</sup>. The thioanions formed are also treated with heavy metal ions such as Zn<sup>2+</sup>, Ni<sup>2+</sup> and Th<sup>4+</sup> to investigate the existence of their different thioantimonite anions.

## Experimental

Merck's guaranteed extra-pure reagents, SbCl<sub>3</sub>, Na<sub>2</sub>S.9H<sub>2</sub>O, CH<sub>3</sub>COOH, Th(NO<sub>3</sub>)<sub>4</sub>.5H<sub>2</sub>O and hydrochloric acid were used and the solutions were prepared with fresh distilled water. The sodium ortho-thioantimonite solution was prepared by carefully digesting one mole of a synthesized sample of Sb<sub>2</sub>S<sub>3</sub> with three moles of Na<sub>2</sub>S. The concentration of the stock solution was further checked by determining antimony as sulfide<sup>9a</sup> and sulfur by the wet process<sup>9b</sup>.

The pH and conductometric measurements were carried out in the usual manner<sup>5</sup>. Using different concentra-

tions of the reactants, a series of glass electrode and conductometric titrations was performed. The observed pH changes were plotted as a function of the volume of the titrant added. The inflections obtained by the curves were confirmed by the pronounced maxima in dpH/dV and zero in d<sup>2</sup>pH/dV<sup>2</sup> graphs. The end-points in conductometric titrations were located graphically. The electrometric titration results from the formation of thioantimonite anions and thorium thioantimonites are summarized in Tables 1 and 2, respectively. Job's method of continuous variation using electrical conductance measurements was also employed for determining the stoichiometry of thioantimonite anions formed by the interaction of acids (HCl and CH<sub>3</sub>COOH) and ortho-thioantimonite. The difference in specific conductivities (the sum of the conductivity of constituent solutions minus the observed specific conductivity of the mixtures) were plotted against the composition of the mixtures. From the maxima obtained in such plots, the stoichiometry of the compound formed was established.

**Table 1.** Summary of the results of the electrometric titrations. Volume of sodium ortho-thioantimonite taken in the cell = 25mL.

Molarity of solutions		Equivalence points (mL) for the formation of					
		Pyro-thioantimonite			Meta-thioantimonite		
HCl	Na <sub>3</sub> SbS <sub>3</sub>	Calc.	A	B*	Calc.	A	B*
M/2	M/30	1.67	1.65	1.70	3.33	-	3.35
M/5	M/80	1.56	1.55	1.55	3.13	-	3.15
M/10	M/125	2.00	2.00	2.00	4.00	-	4.00
M/20	M/175	1.81	1.80	1.80	3.63	-	3.63

\* A and B represent the end-points observed from pH and conductometric titrations, respectively.

**Table 2.** Summary of results of electrometric titrations. Volume of titre solution taken in the cell = 25 mL.

Molarity of Solutions		Equivalence points (mL)			Formula supported
		Calc.	Observed from		
			pH	Conductance	
Th(NO <sub>3</sub> ) <sub>4</sub>	Na <sub>3</sub> SbS <sub>3</sub>	Direct titrations, Fig.3, curves 1 and 2			3ThS <sub>2</sub> .2Sb <sub>2</sub> S <sub>3</sub>
M/10	M/75	2.50	2.50	2.50	
M/20	M/200	1.88	1.86	1.88	
M/40	M/350	2.14	2.14	2.14	
		Reverse titrations, Fig3, curves 3 and 4			3ThS <sub>2</sub> .2Sb <sub>2</sub> S <sub>3</sub>
M/350	M/20	1.90	1.90	1.90	
M/600	M/40	2.22	2.22	2.20	
M/1000	M/60	2.00	2.00	1.98	
Th(NO <sub>3</sub> ) <sub>4</sub>	Na <sub>4</sub> Sb <sub>2</sub> S <sub>5</sub>	Direct titrations, Fig.4			ThS <sub>2</sub> .2Sb <sub>2</sub> S <sub>5</sub>
M/10	M/100	2.50	2.50	2.50	
M/20	M/250	2.00	2.00	2.00	
M/40	M/450	2.22	2.22	2.24	

The precipitates obtained at the end-points of the titrations between thorium nitrate and sodium thioantimonites were also analyzed to substantiate the electrometric results. The different thorium thioantimonites were prepared by mixing stoichiometric amounts of thorium nitrate solution with the respective sodium thioantimonite solutions. The precipitates obtained were washed several times with aqueous 10% (v/v) ethanolic solution and dried in a vacuum dessicator for 40 h. A known amount (2 g) of each of the above was digested with concentrated  $\text{HNO}_3$  (15 mL) to dryness in a steam bath. The treatment was repeated two times. The residue was dissolved in a minimum quantity of hydrochloric acid and then analyzed quantitatively for an-

timony<sup>9c</sup> and thorium<sup>9d</sup>. From the proportions of thorium, antimony and sulfur in the compounds thus obtained, their compositions were established. The results are summarized in Table 3.

## Results and Discussion

### Thioantimonite anions

A perusal of the pH titration curves (Fig. 1A) indicated that the addition of one mole of acid ( $\text{HCl}$  and  $\text{CH}_3\text{COOH}$ ) per mole of  $\text{Na}_3\text{SbS}_3$  yields a pronounced inflection in the region of pH 8.7-9.1, corresponding to the formation of the pyrothio anion  $\text{Sb}_2\text{S}_5^{4-}$ . Further addition of the acids yields one more inflection, showing the consumption of three

Table 3. Summary of analytical results.

Proposed formula of the compound	Mode of synthesis	Analysis %: Found (Calculated)		
		Th	Sb	S
Analysis of the ortho-thioantimonite precipitates				
$3\text{ThS}_22\text{Sb}_2\text{S}_3$	Direct*	44.36 (44.40)	31.09 (31.06)	24.56 (24.54)
	Reverse	44.43	31.02	24.51
Analysis of the pyro-thioantimonite precipitates				
$\text{ThS}_2\text{Sb}_2\text{S}_3$	Direct	36.53 (36.49)	38.24 (38.29)	25.20 (25.22)

\*Direct - Thorium nitrate solution added to sodium ortho-thioantimonite solution. Reverse - sodium ortho-thioantimonite solution added to thorium nitrate solution.

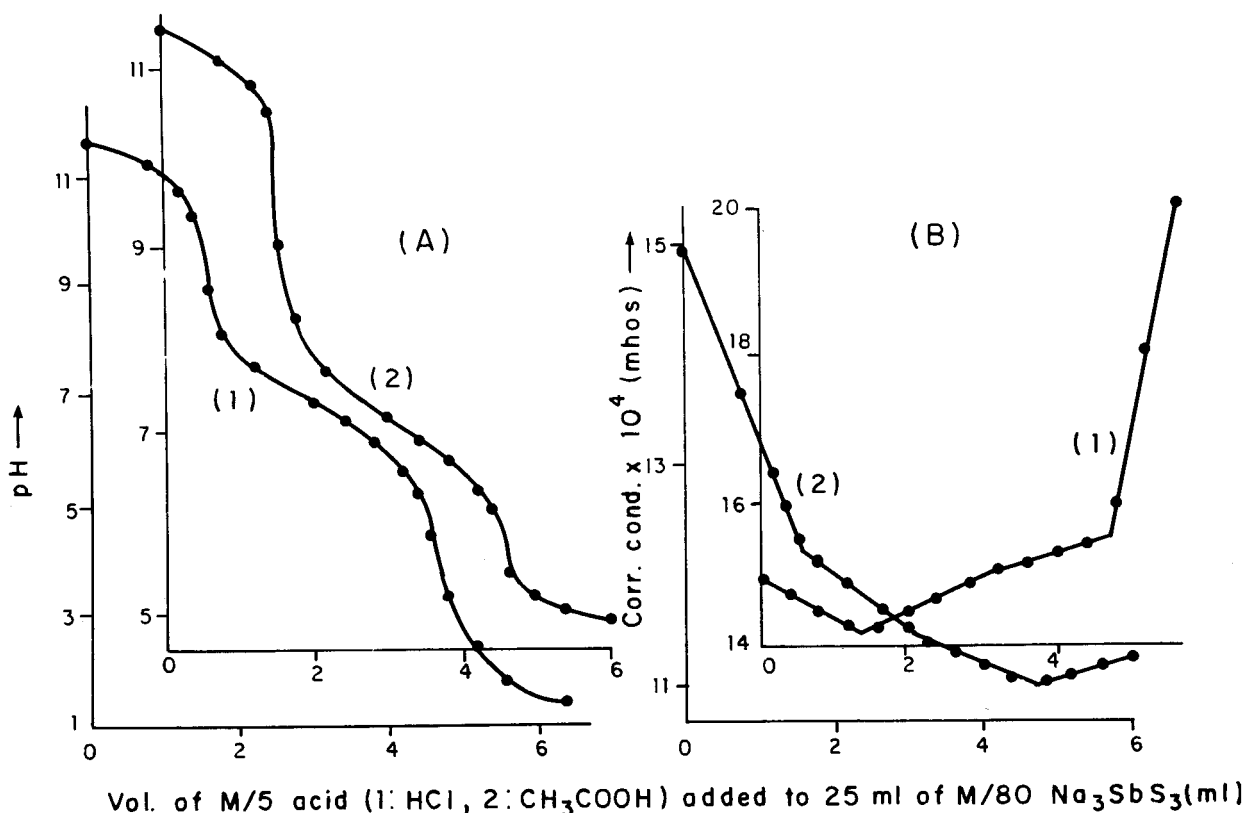
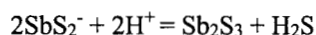
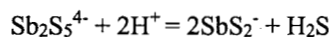
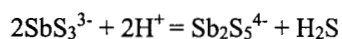


Figure 1. (A) pH and (B) conductometric titrations.

moles of  $H^+$  per mole of  $SbS_3^{3-}$ , corresponding to the precipitation of  $Sb_2S_3$  in the pH range of 4.0-5.0. The pH value of such acidified solutions became steady only after a lapse of some time indicating that the reaction proceeds by way of some unstable intermediate species. It was noted that the reaction was faster in case the of strong acid (HCl).

Conductometric titrations between the acids (HCl,  $CH_3COOH$ ) and  $Na_3SbS_3$  were also carried out using similar concentrations of the reagents for the sake of comparing results. The observed breaks (Fig. 1B) confirm the formation of  $Sb_2S_5^{4-}$  and  $Sb_2S_3$ , as indicated by the studies, and in addition, gave one more break at the ratio  $H^+ : SbS_3^{3-}$  as 1:2 suggesting the formation of the meta-thioantimonite anion,  $SbS_2^-$ , in the range of pH 6.6-7.1. A similar meta-anion of As(III) was not evidenced by this study<sup>7</sup>.

Job's method of continuous variation gave one sharp maxima (Fig. 2) at a molar ratio of  $H^+ : SbS_3^{3-}$  as 2:1, confirming the formation of meta-thioantimonite. The step-by-step degradation of ortho-thioantimonate upon acidification can be shown as follows:



The results of the electrometric experiments on the acid orthoantimonite system suggest the formation of alkali pyro-, and meta-thioantimonite before the final decomposition into  $Sb_2S_3$  at pH ranges of 8.7-9.1 and 6.6-7.1, respectively. Gravimetric investigations were performed on the orange precipitate obtained, which confirmed the composition to be  $Sb_2S_3$ .

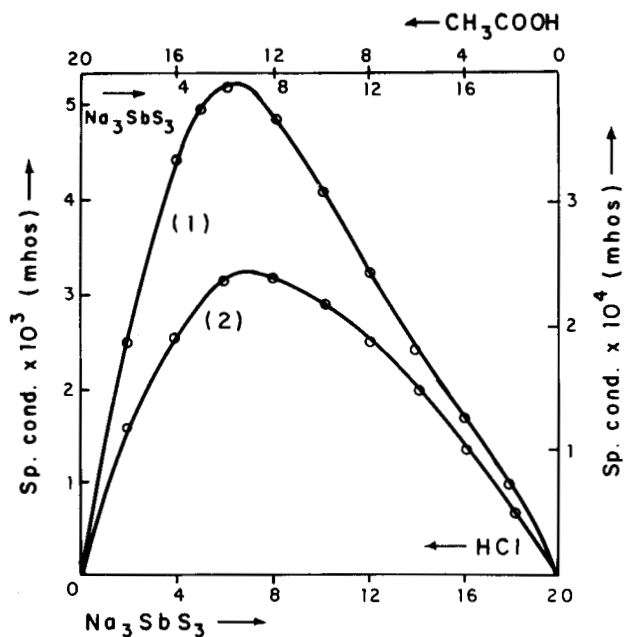
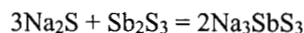


Figure 2. Continuous variation study by Job's method. 1: M/50 HCl vs. M/50  $Na_3SbS_3$ . 2: M/100  $CH_3COOH$  vs. M/100  $Na_3SbS_3$ .

### Thorium thioantimonites

The solution of sodium ortho-thioantimonite (pH 11.5) was prepared by digesting an analyzed sample of antimony trisulfide in a sodium sulfide solution of the required strength.



Sodium pyro-thioantimonite (pH 8.9) and meta-thioantimonite (pH 6.8), as suggested by the above studies, were prepared by progressive additions of hydrochloric acid to sodium ortho-thioantimonite solutions in the molar ratios of 1:1 and 1:2, respectively.

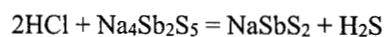
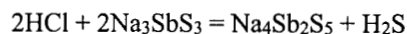


Figure 3 illustrates the curves of the pH and conductometric titrations performed between the solutions of sodium ortho-thioantimonite and thorium nitrate. In direct titrations (curve 1), when  $Th(NO_3)_4$  (pH 3.4) solution was added to the ortho-thioantimonite solution (pH 11.5) a sharp fall in pH was noted with an inflection at the molar ratio of  $Th^{4+} : SbS_3^{3-}$  as 3:4 in the vicinity of pH 6.1, corresponding to the stoichiometry for the formation of thorium

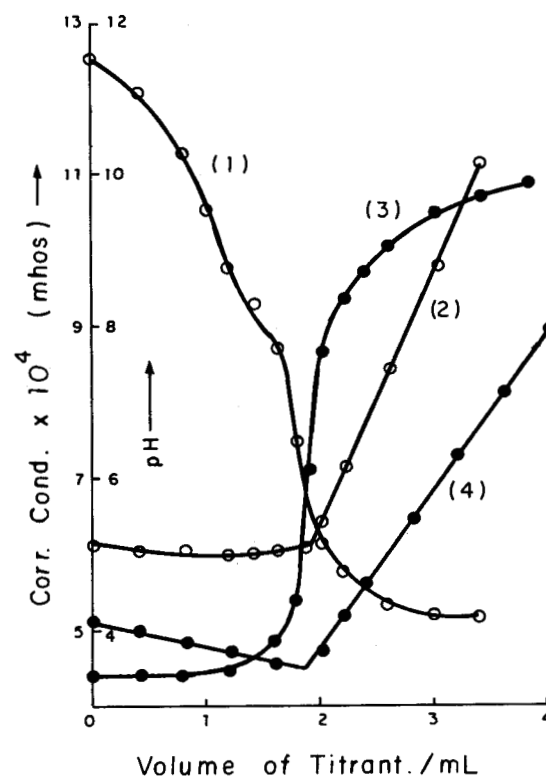
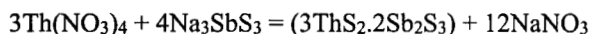


Figure 3. Ortho-thioantimonite titrations. Curves (1) and (2): M/20  $Th(NO_3)_4$  added to 25 mL. of M/200  $Na_3SbS_3$ . Curves (3) and (4): M/20  $Na_3SbS_3$  added to 25 mL. of M/350  $Th(NO_3)_4$ .

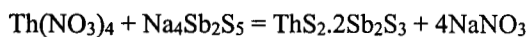
ortho-thioantimonite,  $3\text{ThS}_2 \cdot 2\text{Sb}_2\text{S}_3$ . In reverse titrations (curve 3) when  $\text{Na}_3\text{SbS}_3$  solution was added to the thorium nitrate solution, the pH first increased very slowly, but at the end-point it jumped corresponding to the formation of the same compound in accordance with the following equation.



Employing similar concentrations of the reactants, both direct (curve 2) and reverse (curve 4) conductometric titrations between thorium nitrate and sodium ortho-thioantimonite gave well-defined breaks at a 3:4 molar ratio of  $\text{Th}^{4+}:\text{SbS}_3^{3-}$ , confirming the formation of thorium ortho-thioantimonite.

An interesting phenomenon was observed in both the pH and conductometric direct titrations, when thorium nitrate was used as titrant. The pH and conductance value took a longer time to stabilize in the region of the molar ratio of  $\text{Th}^{4+}:\text{SbS}_3^{3-}$  as 1:2, which may be ascribed to the formation of an intermediate species  $\text{ThS}_2 \cdot \text{Na}_2\text{S} \cdot \text{Sb}_2\text{S}_3$  before precipitation of the final stable product  $3\text{ThS}_2 \cdot 2\text{Sb}_2\text{S}_3$ . Sb(V) has been reported to form such an intermediate compound with thorium<sup>10</sup>.

Figure 4 illustrates the changes occurring in the pH and conductance values when  $\text{Th}(\text{NO}_3)_4$  solution is added to sodium pyro-thioantimonite solution. The titration curves provide well-defined inflections and breaks at the point where the molar ratio of  $\text{Th}^{4+}:\text{Sb}_2\text{S}_5^{4-}$  is 1:1, which corresponds to the stoichiometry for the formation of  $\text{ThS}_2\text{Sb}_2\text{S}_3$  in the neighborhood of pH 5.2 (Table 1). The reaction can be represented by the following equation.



Investigations on the reaction of thorium nitrate with sodium meta-thioantimonite failed to give any dependable results. This may be ascribed to the soluble nature of the product, the small difference in the pH values of the reactants, and presence of sodium chloride in appreciable amounts, preventing the occurrence of breaks in the titration curves.

The results of the quantitative elemental analysis of the precipitates by classical methods were used to calculate the proportions of the elements present in the compounds. From these proportions, the composition of the compounds were established which were found to be the same as those obtained by the electrometric techniques (see Table 3).

Similar investigations on the formation of thioantimonites of zinc<sup>8</sup> and nickel confirmed the formation of  $3\text{ZnS} \cdot \text{Sb}_2\text{S}_3$  (pH 7.3) and  $2\text{ZnS} \cdot \text{Sb}_2\text{S}_3$  (pH 5.2), and  $3\text{NiS} \cdot \text{Sb}_2\text{S}_3$  (pH 8.9) and  $2\text{NiS} \cdot \text{Sb}_2\text{S}_3$  (pH 7.8), respectively.

## Conclusions

The results of the electrometric study suggest the formation of  $\text{Sb}_2\text{S}_5^{4-}$  and  $\text{SbS}_2^-$  in the pH ranges of 8.7-9.1 and

6.6-7.1, respectively, before the final decomposition of  $\text{SbS}_3^{3-}$  into  $\text{Sb}_2\text{S}_3^{11}$ . The electrometric and analytical investigations indicate the formation of ortho- $3\text{ThS}_2 \cdot 2\text{Sb}_2\text{S}_3$  and pyro- $\text{ThS}_2 \cdot \text{Sb}_2\text{S}_3$  thioantimonites in the neighborhood of pH 6.1 and 5.2, respectively.

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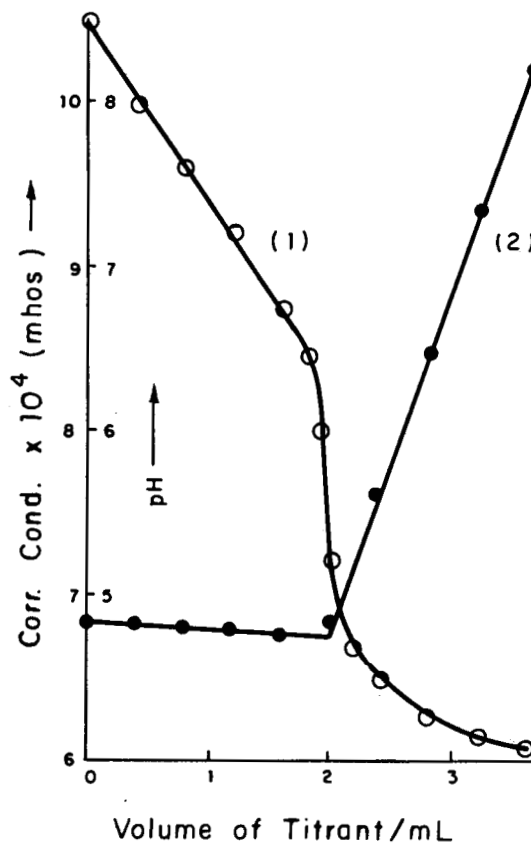


Figure 4. Pyro-thioantimonite titrations. M/20  $\text{Th}(\text{NO}_3)_4$  added to 25 mL of M/250  $\text{Na}_3\text{SbS}_3$ .

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