Polarographic Determination of Tin and Antimony in Iron and Steel

Polarographic Determination of Tin and Antimony in Iron and Steel*

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Synopsis

For the estimation by ploarography of small amounts of tin and antimony contained as impurities in iron and steel, it was necessary to remove the effect of interference of iron. These impurities were, therefore, separated from iron by co-precipitating with manganese dioxide. The precipitate was decomposed with hydrochloric acid and hydrogen peroxide, and tin was reduced with aluminium foil to Sn^{2+} and its polarogram was taken in ammonium chloride solution. Antimony solution was heated with sulfuric acid till the evolution of white fume to reduce it to Sb^{3+} and the polarogram was taken in 0.1N hydrochloric acid. 0.02～0.1 per cent of tin and 0.005～0.1 per cent antimony in iron and steel could be determined.

I. Introduction

In a usual chemical analysis, tin or antimony contained in iron and steel as impurity is separated from iron as sulfide and then determined volumetrically, such as iodometry for tin and permanganate method for antimony. As these methods are very confused and time-consuming, the excellent photometric methods have recently been proposed by Gotô and Kakita, in which tin is determined with cacotheline(1) and antimony is done with methyl violet-amylacetate extraction method(2) after both are separated from iron by the co-precipitation with manganese dioxide. In the present research, polarographic determinations of tin and antimony in iron and steel were investigated.

II. Experimental method

In the case of polarographic analysis of the elements in iron and steel, iron in trivalent state interferes greatly with them, as the current caused by $Fe^{3+} \rightarrow Fe^{2+}$ is observable at the voltage near zero. So the reduction of Fe^{3+} to Fe^{2+} or the removal of iron is necessary before measuring polarogram of element.

In the present research, as it was difficult to reduce large amounts of iron, tin and antimony were first separated from large amounts of iron by co-precipitation with manganese dioxide and small amounts of iron accompanied with precipitation were reduced by aluminium foil or hydrazine sulfate, and then the suitable conditions for the polarographic determination of tin and antimony in iron and steel were examined.

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* The 869th report of the Research Institute for Iron, Steel and Other Metals.
This report has been published in the Japan Analyst, **3** (1954), 320 (in Japanese).

(1) H. Gotô and Y. Kakita, Sci. Rep. RITU, **A5** (1953), 554; **A6** (1954), 12.
(2) H. Gotô and Y. Kakita, Sci. Rep. RITU, **A4** (1952), 589.

III. Reagent and concentration

1. Stannous chloride solution.

Metallic tin was dissolved in 6N hydrochloric acid solution, and stock solution was prepared with the concentration of tin 1.0 mg/ml in 6N hydrochloric acid.

2. Metallic antimony was dissolved in concentrated sulfuric acid, and the stock solution was prepared with the concentration of Sb^{3+} 1.0 mg/ml in 6N hydrochloric acid.

3. Ferric chloride and ferric sulfate solutions were prepared by dissolving electrolytic iron in hydrochloric acid or sulfuric acid and oxidized with hydrogen peroxide and then diluted with distilled water to keep the concentration of iron at 100 mg/ml and acid concentration at 1N.

4. Aluminium foil.

Chemically pure foil or the foil for rapping the tobacco was used.

5. Ammonium chloride and hydrazine sulfate were all chemically pure reagents, and 20 per cent manganese sulfate or manganese chloride solution was made by dissolving chemically pure $MnSO_4 \cdot H_2O$ or $MnCl_2 \cdot 4H_2O$.

6. Gelatine of 0.20 per cent aqueous solution was used.

7. 6N of hydrochloric acid or sulfuric acid were used.

IV. Instrument and dropping velocity of mercury electrode

The instrument made by Yanagimoto, was used for the measurement of polarogram, and double walled polarographic cell was used to hold the temperature of the test solution constant by passing temperature-controlled water through the walls. The dropping velocity of mercury electrode was of 4.5 sec interval between successive drops.

V. Determination of tin

1. Experimental procedure

Although double wave could be obtained,[3][4][5] in the polarography of Sn^{4+} in hydrochloric acid the measurement became impossible when Sb^{3+} was present. When the polarogram was measured after tin was reduced to Sn^{2+} by aluminium foil in hydrochloric acid solution, the successful diffusion current-voltage curve was obtained at the half wave potential of -0.47 V versus saturated calomel electrode without the interference of antimony as it was reduced to metallic state. On the other hand, it might be expected that an appreciable amount of manganese chloride was forced to present as one of the components of supporting electrolyte, owing to the adoption of the co-precipitation procedure by manganese dioxide for the separation of tin and antimony from iron. Then, the examination of various conditions was carried out as follows: In the solution containing tin as stannic chloride, manganese chloride and 0.2 g of aluminium foil were added and heated

(3) J. J. Lingane, Ind. Eng. Chem. Anal. Ed., **15** (1943), 588.
(4) J. J. Lingane, ibid., **16** (1944), 147.
(5) A. S. Shapor, J. Applied Chem. U.S.S.R., **12** (1939), 1555.

in CO_2 atmosphere to reduce tin, and then the total volume was made to 50 ml, after 2 ml of 0.2 per cent gelatine solution was added. An aliquot volume of this well-mixed solution was taken in a polarographic cell and hydrogen gas was passed through it for 10 min to expell dissolved oxygen and then the polarogram of tin was measured at the voltage ranging from −0.3 to −0.7 V.

2. Concentration of hydrochloric acid

With the above procedure, the influeneces of the concentration change of hydrochloric acid on the polarographic wave height of tin were observed and the result is shown in Table 1. In the concentration range of 0.7 ~2.0 N of hydrochloric acid, no change in wave height was obtained, but in the less concentration than 0.5 N the wave height became less and in the higher one than 2.5 N the diffusion current did not became stationary. So 1.0 N of hydrochloric acid concentration was found to be suitable.

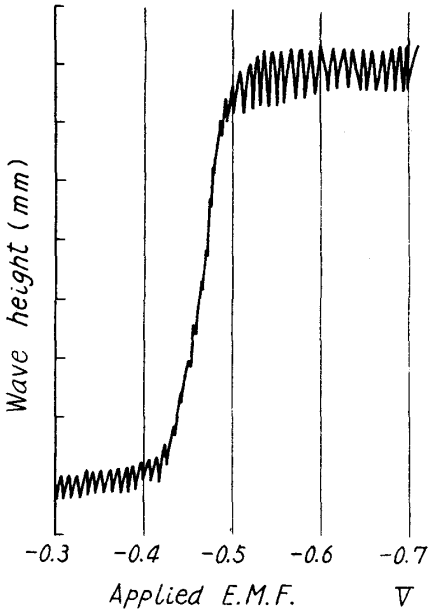

Fig. 1. The polarograph of Sn^{2+}.
The solution contained 35 mg of Sn, 10 ml of 20% $MnCl_2$ solution, 2 ml of 0.2 % gelatine and aluminium 0.2 g in 50 ml of 1.0 N HCl solution.

Table 1. Influences of the concentration of HCl on the wave height of tin.

The concentration of HCl (N)	Wave height (mm)	
0.5	87.5	87.0
0.7	88.4	88.0
1.0	88.2	88.5
1.5	88.5	88.5
2.0	88.4	88.0
2.5	88.0	87.2
3.0	86.1	86.6*

The solution contained 5mg of Sn, 10 g of NH_4Cl, 10 ml of 20 % $MnCl_2$ solution, 0.2 g of aluminium and 2 ml of 0.2 % gelatine in total volume of 50ml.
Temperature; 20°C.
* the current change became irregular.

3. Amount of ammonium chloride

10 ml of 20 per cent $MnCl_2$ solution and various amounts of ammonium chloride were added to the 1.0 N of hydrochloric acid solution, and the wave height of polarograph of tin was measured. From the results the suitable amount of ammonium chloride to be present in the solution for the determination of tin was found to be 8~13 g in the volume of 350 ml.

4. Amount of manganese chloride

When various amounts of manganese chloride solution were added, no change

in the polarographic wave of tin was found, and so the amount of manganese chloride which would be introduced in the solution from the manganese dioxide precipitation procedure was controlled to be 4 per cent in the final volume of the sample solution.

5. Preparation of calibration curve of tin

10 g of ammonium chloride, 10 ml of 20 per cent manganese chloride solution and 0.2 g of aluminium foil were added to the solution containing various amounts of tin, and tin was reduced in CO_2 atmosphere. 0.2 per cent of gelatine was added to it after cooling, until the total volume was made to 50 ml, and then the polarogram of tin was measured. The polarographic wave height obtained was proportional to the amount of tin as shown in Fig. 2.

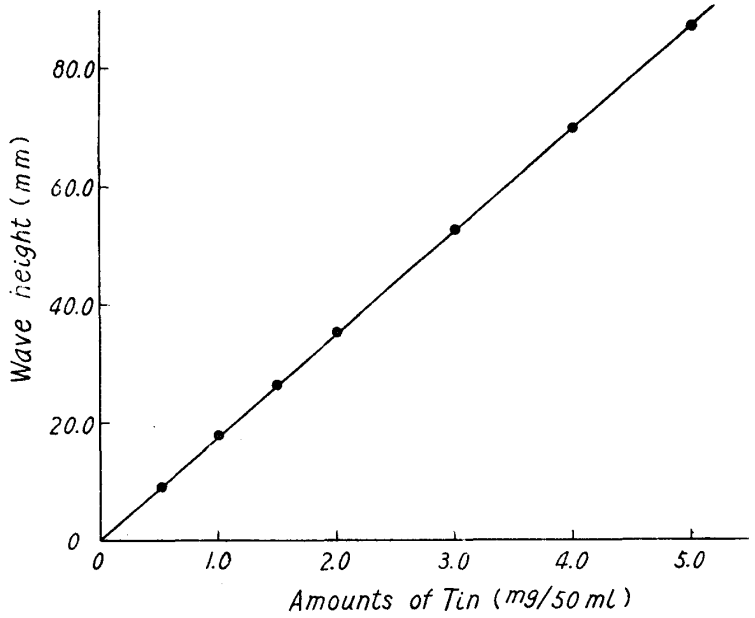

Fig. 2. Calibration curve of tin.
The solution contained 10 g of NH_4Cl, 10 ml of 20 % $MnCl_2$ solution, 0.2 g of Al and 2 ml of 0.2 % gelatine in 50 ml of 1.0 N HCl solution at 20°C.

6. Influences of diverse ions

When tin was separated with manganese dioxide from iron, arsenic, antimony and small amount of iron were accompanied with the precipitate. Then the influences of the presence of small amounts of these elements on the polarogram of tin were investigated by adding 2.0 mg of antimony, 5.0 mg arsenic and 50 mg of iron in 50 ml of tin solution, but no influence was observed, as arsenic and antimony were reduced to metallic state and iron to divalent state by aluminium.

VI. Determination of antimony

1. Experimental procedure

Although the polarogram of antimony was successfully obtained in hydrochloric acid solution, it was impossible to determine antimony in hydrochloric acid solution in the presence of tin, because of overlapping of the wave of Sn^{4+} to Sb^{3+}

wave near the voltage of −0.1 V. In sulfuric acid solution, the polarographic wave of Sb^{3+} revealed appreciably dull curve and the diffusion current did not become stationary, but in the presence of small amounts of hydrochloric acid, the good reproducible polarographic wave was obtained with the half wave potential of −0.23 V versus to saturated calomel electrode. Then, the polarographic determination of antimony was investigated by using this solution with following condition; 1 mg of antimonous sulfate solution (1.0 mg Sb^{3+}) was taken and sulfuric acid, hydrochloric acid, manganese sulfate solution and 1 ml of 0.2 per cent gelatine solution were added and total volume was made 25 ml.

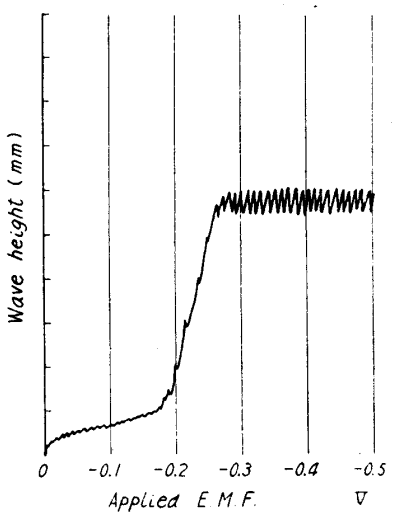

Fig 3. The polarograph of Sb^{3+}. The solution contained 0.75 mg of Sb^{3+}, 20 ml of 20% $MnCl_2$ solution and 1 ml of 0.2 % gelatine in 25 ml of 0.1N HCl and 1.0N H_2SO_4 solution.

After mixing this solution well, and transferring an aliquot volume of it to the polarographic cell, hydrogen gas was passed through the solution for 10 min and then polarogram of antimony was measured at the voltage between 0 ~ −0.4 V.

2. Concentration of sulfuric acid

In the above experimental condition, the concentration of sulfuric acid added was changed and the change in polarographic wave height of antimony was observed. The result is shown in Table 2, from which it will be seen that the concentration change of sulfuric acid from 1.0 to 2.0 N has no effect, and that the change less than 0.7 N caused to produce a complicated wave and so sulfuric acid should be kept at the concentration of 1.0 N.

Table 2. Influences of H_2SO_4 on the wave height of antimony.

The concentration of H_2SO_4 (N)	Wave height (mm)	
0.5	54.2	53.1
0.7	54.3	54.8
1.0	54.0	54.6
1.5	53.8	54.2
2.0	54.3	54.0

The solution contained 1 mg of Sb, 20 ml of 20 % $MnSO_4$ solution, 1 ml of 0.2 % gelatine in total volume of 250 ml of 0.1 N HCl solution.
Temp.; 20°C.

3. Concentration of hydrochloric acid

Various amounts of hydrochloric acid were added to the sulfuric acid solution of 1.0 N containing 20 ml of 20 per cent manganese sulfate, and the total volume was brought to 25 ml and then the polarogram of antimony was measured. From the result obtained, it was seen that in the range from 0.1 to 0.2 N of hydrochloric

acid the polarographic wave height of antimony was not changed as shown in Table 3, and that in the concentration less than 0.05 N current became gradually less and in the higher concentration than 0.25 N the wave height became to increase. So the concentration of hydrochloric acid added was kept at 0.1 N.

Table 3. Influence of HCl on the wave height of antimony.

The concentration of HCl (N)	Wave height (mm)	
0.05	52.2	51.1
0.10	54.2	54.8
0.15	53.8	54.3
0.20	54.0	54.6
0.25	55.2	55.9
0.30	57.2	58.0

The solution contained 1 mg of Sb, 20 ml of 20 % $MnSO_4$ solution 1 ml of 0.2 % gelatine in 25 ml of 1.0 N H_2SO_4 solution.
Temp.; 20°C.

4. Amount of manganese sulfate

There was found no influence of the change in the concentration of manganese sulfate which might be introduced in the solution by the precipitation procedure with manganese dioxide. So manganese was added as much to keep its final concentration at 16 per cent as manganese sulfate.

5. The calibration curve of antimony

Under these conditions obtained above, the calibration curve of antimony was measured at 25°C with the solution of various concentrations of antimony containing sulfuric acid (1.0 N), hydrochloric acid (0.1 N) and manganese sulfate (16 per cent), and a linear relation was obtained between the diffusion current of antimony (Sb^{3+}) and its amount as shown in Fig. 4.

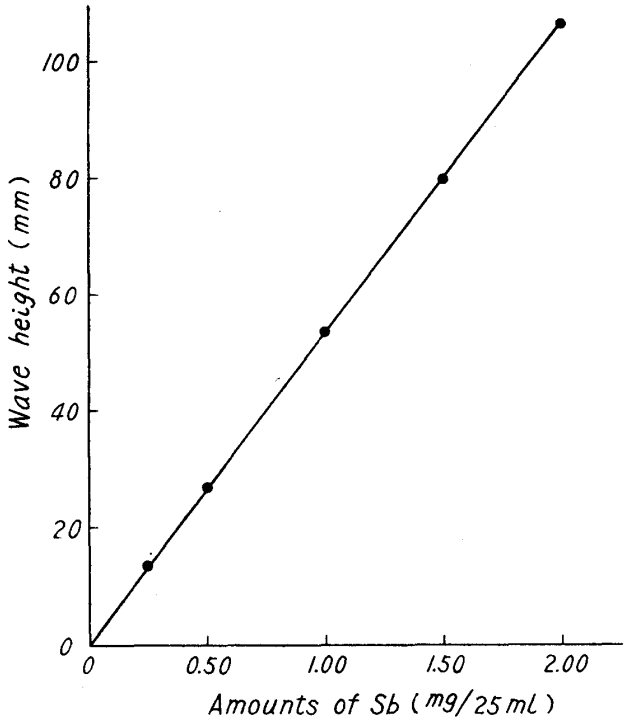

Fig. 4. Calibration curve of antimony.
The solution contained 20 ml of 20 % $MnCl_2$ solution and 1 ml of 0.2% gelatine in 25 ml of 0.1 N HCl and 1.0 N H_2SO_4 solution at 20°C.

6. Influences of diverse ions

(i) Influences of tin and arsenic

When antimony was separated by manganese dioxide from iron, tin and arsenic might be accompanied with it if they were presents, and so the polarogram was measured by adding various amounts of tin and arsenic to the antimony solution. But it was not found any interfererce of them with the

polarography of antimony even in the presence of 5 mg of them in 25 ml of sample solution, though arsenic was reduced at the voltage near −0.5 V.

Table 4. Influences of tin or antimony on the wave height of antimony.

Sn^{4+} added (mg/ml)	Wave height (mm)		As^{3+} added (mg/ml)	Wave height (mm)	
0	54.3	55.0	0	54.6	54.0
0.04	53.9	54.8	0.05	54.0	54.5
0.08	54.0	54.6	0.10	54.1	53.8
0.15	54.5	54.6	0.15	55.0	54.5
0.20	55.0	54.5	0.20	54.8	54.2

The solution contained 1 mg of Sb^{3+}, 20 ml of 20% $MnSO_4$ solution, 1 ml of 0.20% gelatine in 25 ml of 1.0 N H_2SO_4 and 0.1 N HCl solution.
Temp.; 20°C.

(ii) Influences of iron

A small amount of iron might be accompanied with antimony in manganese dioxide precipitate, while iron was often reduced by hydrazine sulfate in a usual polarographic procedure. So the following experiment was made to avoid the interference of it. The polarogram of antimony was measured first in the presence of 0.5, 1.0 or 2.0 g of hydrazine sulfate and no change was found in the polarographic wave of antimony. Next, it was measured in the presence of ferrous ion which was produced by reducing various amounts of ferric sulfate solution (Fe^{3+} 10.0 mg/ml) by 1 g of hydrazine sulfate. From the results shown in Table 5, it

Table 5. Influence of Fe^{3+} on the wave height of Sb^{3+}.

Amounts of Fe^{3+} added (mg/ml)	Wave height of Sb			
	When Sn^{4+} and As^{3+} was contained		When Sn^{4} and As^{3+} was absent	
0	54.8	55.2	54.6	55.1
0.1	55.0	55.0	55.3	54.8
0.5	54.3	54.8	54.2	54.8
1.0	55.2	54.6	54.6	55.0
1.5	55.0	55.4	55.0	55.4

i) The solution contained 1mg of Sb^{3+}, 20 ml of 20% $MnSO_4$ solution 1.0 g of hydrazine sulfate and 1 ml of 0.2% gelatine in 25 ml of 1.0 N H_2SO_4 and 0.1 N HCl solution.
ii) Amounts of Sn^{4+} and As^{3+} added were 5.0 mg in each.
iii) Temp.; 20°C.

was seen that even in the presence of 37.5 mg of iron in 25 ml of solution no change was seen in the polarogram of antimony, and so 1 g of hydrazine sulfate was found to be sufficient to reduce iron being accompanied. When ferric sulfate solution was added to the solution containing 1 mg of antimony, 5 mg of tin and 5 mg of arsenic and reduced by heating 1 g of hydrazine sulfate and then the polarogram for antimony was measured, the result was also the same as above, and the change in the diffusion current caused by the interferences of their elements was not found as shown in Fig. 5.

VII. Procedure for the determination of tin and antimony in iron and steel

From the results obtained above, the following procedures were established for the polarographic determination of tin and antimony in iron and steel.

1. Determination of tin

5 g of sample are taken in 500 ml of beaker and dissolved with 120 ml of nitric acid (1 + 2), and 150 ml of hot water and 10 ml of 20 per cent manganese sulfate solution are added to it and boiled. Then, 5 ml of 1 N potassium permanganate solution are added dropwise to the solution being on the boil and manganese dioxide is precipitated completely. After standing for 5~7 min to cool, manganese dioxide is filtered and washed with hot water and the precipitate is transferred to the previous beaker as much as possible from the filter paper and 3 N of hot hydrochloric acid solution and small amounts of hydrogen peroxide are added to the residual on the paper and the filtrate is received in the beaker. Filter paper is washed completely with hot water and washing water is added to the filtrate. The filtrate in the beaker is boiled to decompose excess hydrogen peroxide after the precipitate is dissolved completely and then evaporated to 20 ml. This solution is transferred to the 100 ml Erlenmayer's flask, and 10 g of ammonium chloride and 0.2 g of aluminium foil are added in it and the solution is heated in CO_2 atmosphere so that tin may be reduced, until excess of aluminium is dissolved completely and large bubbles begin to produce. Then, the solution is cooled in CO_2 atmosphere with water and transferred to 50 ml volumetric flask, and 2 ml of 0.2 per cent gelatine is added to it, and then it is made to 50 ml exactly. An aliquot volume of this well-mixed solution is taken in the polarographic cell and the polarogram of tin is measured at the voltage between -0.3~0.7 V after hydrogen or nitrogen gas is passed through it to expel oxygen completely. Tin is determined from the polarographic wave height obtained at the half wave potential of -0.47 V versus saturated calomel electrode and from the calibration curve obtained previously.

2. Determination of antimony

5 g of sample taken in 500 ml beaker is dissolved with 120 ml of nitric acid (1 + 2), and antimony is co-precipitated with manganese dioxide as mentioned in the case of tin and washed well. After the precipitate is transferred to the beaker previously used as much as possible, 10~15 ml of hot 6 N sulfuric acid and solution and small amount of hydrogen peroxide are added to the residue on the filter paper and the filtrate is received with the beaker containing the most of the precipitate in order to dissolve all of it. The filter paper is washed well with hot water and the washing water is taken in the beaker too. Then, the solution in the beaker is boiled to decompose the excess of hydrogen peroxide and evaporated to fumes of sulfuric acid. After cooling, 5 ml of sulfuric acid and small amounts of water are added to dissolve the salt deposited, and iron is reduced by heating the solution with 1 g of hydydrazine sulfate. 1 ml of 3 N of hydrochloric acid and 1 ml of 0.2 per

cent gelatine are added to it after cooling, and the solution is made to 25 ml by volumetric flask and mixed well. An aliquot volume of it is taken in the polarographic cell, and hydrogen or nitrogen gas is passed through it to expel dissolved oxygen for 10 min, and then the polarogram of antimony is measured at the voltage between 0～−0.4 V. Antimony is determined from the polarographic wave height at the half wave potential of −0.23 V versus saturated calomel electrode and the calibration curve obtained previously.

VIII. The results of the polarographic determination of tin and antimony in iron and steel sample

The synthetic samples made from 5 g of electrolytic iron and various amounts of tin or antimony were first analysed with the procedure described above, the results of which are shown in Table 6. Next, tin in the routine steel sample were determined polarographically and photometrically with cacotheline or by iodometry after isolating with hydrogen sulfide, and the results are shown in Table 7. As the sample containing antimony could not be in hand, antimony was added to the routine steel samples containing tin and the polarographic determination was made as above. The results are shown in Table 7.

Table 6. Polarographic determination of tin and antimony in synthetic samples of iron.

Sn added (mg)	Sn determined (mg)		Sb added (mg)	Sn determined (mg)	
0.50	0.54	0.51	0.10	0.10	0.09
2.50	2.53	2.44	0.25	0.26	0.21
5.00	5.01	5.08	0.50	0.53	0.46

Table 7. Comparison of the results of polarographic determination of tin or antimony in iron and steel with the results obtained by other methods.

Sample	The results of Sn (%)		The results of Sb (%)	
	Chemical analysis	Polarographic method	Amount added[a]	Polarographic method
Steel (I)	0.038 0.032[b]	0.035 0.031	0.005	0.0046 0.0052
Steel (II)	0.025[c]	0.023 0.021	0.005	0.0046 0.0048
Steel (III)	0.064[c]	0.059 0.063	0.005	0.0045 0.0056
Steel containing arsenic (I)	0.048[c]	0.046 0.052	0.010	0.0096 0.0092
Steel containing arsenic (II)	0.048[c]	0.046 0.052	0.010	0.0095 0.0084
Steel	0.110[b]	0.091 0.113	0.010	0.0096 0.0087

a) Antimony was added in the steel sample.
b) Iondometric determination.
c) Photometric determination.

Summary

(1) Methods for the polarographic determination of tin and antimony in iron and steel were researched.

(2) Tin was reduced to Sn^{2+} by aluminium foil and polarographed in the supporting electrolyte containing ammonium chloride, manganese chloride and hydrochloric acid.

(3) Antimony was reduced to Sb^{3+} by fuming with sulfuric acid and polarographed in the supporting electrolyte containing manganese sulfate, hydrochloric acid and sulfuric acid.

(4) Tin and antimony in iron and steel were separated from large amounts of iron by precipitation with manganese dioxide.

(5) By the present procedures, 0.02~0.1 per cent of tin and 0.005~0.01 per cent of antimony in iron and steel could be determined polarographically with good reproducibility.