A New Method of Spectrophotometric Determination of Tin with Alizarin Blue : Application of this Method for the Estimation of Tin in Steel and Nonferrous Alloys

A New Method of Spectrophotometric Determination of Tin with Alizarin Blue.
Application of this Method for the Estimation of Tin in Steel and Nonferrous Alloys*

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(Received September 25, 1961)

Synopsis

A new spectrophotometric determination of tin was investigated. Stannic ion formed a colored complex compound with alizarin blue in 1 N-hydrochloric acid solution and was extracted by the mixed solution of cyclohexanone and ethyl acetate. The absorption spectrum of this complex had a maximum absorption at the wave length of 580 mμ, and its molecular absorption coefficient was 9.5×10^3. This reaction was also applied to the determination of tin in steel after separating it with hydrogen sulfide. Similarly, 0001~ 0.1 per cent of tin in nonferrrous alloys was analyzed after being separated by co-precipitation with manganese dioxide.

I. Introduction

Hitherto, it was recognized that alizarin blue reacts, in some ranges of pH, on zinc ion, copper ion and other metal ions by the formation either of complex compounds giving the light absorption at 500–600 mμ, or of the precipitation[1]. The present author found that stannic ion could react on alizarin blue in hydrochloric acid solution and formed violet complex compound. The spectrophotometric measurement of the absorbancy of this compound was applied to the determination of tin. This method quite differing from the hematoxyline method in the determination of stannic ion had a better sensitivity and hardly interfered with antimony and arsen. However, molybdenum, vanadium and iron gave violent interference; in these ions, iron (III) and vanadium could be separated by using hydrogen sulfide.

Manganese did not interfere with this reaction, so that tin in nonferrous alloys could be isolated with manganese dioxide.

By using these separating procedures, tin in steel and in some nonferrous alloys was estimated in good agreement with other methods.

II. Reagents and apparatus

1. Reagents

Alizarin blue extraction solution. After alizarin blue of 0.100 g had been

(1) K. Hirokawa, I. Japan Inst. Metals, **23** (1959), 698.

dissolved in 500 ml of cyclohexanone, 500 ml of ethyl acetate was added and mixed well.

1 N and 12 N hydrochloric acid were used. 50 per cent tartaric acid solution in 1 N hydrochloric acid, 3 per cent potassium permanganate solution and 5 per cent manganese sulfate solution were prepared.

Tin standard solution was made by dissolving tin metal in hydrochloric acid and sulfuric acid. After fuming of sulfuric acid by heating the solution, the standard solution of tin, that is, 1 mg tin per ml in 6 N hydrochloric acid was prepared. This solution was kept as stock solution and diluted with 3 N hydrochloric acid when used.

2. Apparatus

Hitachi spectrophotometer of the type EPU-2 with cells of 1 cm was used.

III. Absorption curve and influence of acid concentration

50 μg stannic ion was put into separatory funnel, and diluted to 20 ml of 2 N hydrochloric acid solution. 10 ml of alizarin blue extraction solution was added to the tin solution and shaken well. By using extracted layer the absorption curve of tin compound was prepared as shown in Fig. 1. From this figure, it was recognized that tin complex had the maximum absorption at 580 mμ.
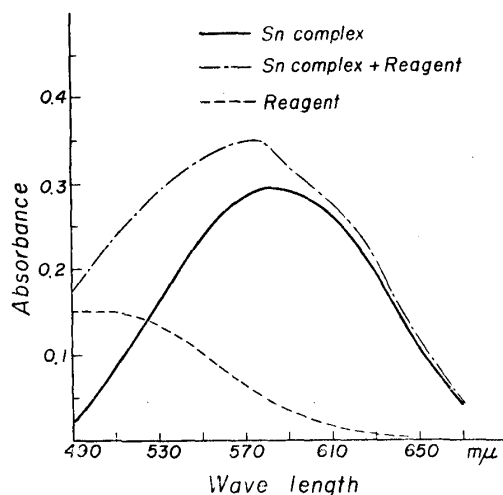

Fig. 1. Absorption Curve

In this case, in order to determine the acidity at which the tin was quantitatively extracted, next experiments were carried out. 50 μg of tin was put in a separatory funnel. The acidity of the solution was adjusted as shown in Fig. 2, and made up to 20 ml. The extractant of 10 ml was added, and shaken to extract tin in organic layer. Similarly an aqueous solution of hydrochloric acid with the same concentration was extracted in the absence of tin and used as blank test solution. These results are shown in Fig. 2, and the maximum absorbance was obtained in the 0.5 N~1.5 N of hydrochloric acid solution. These absorbances
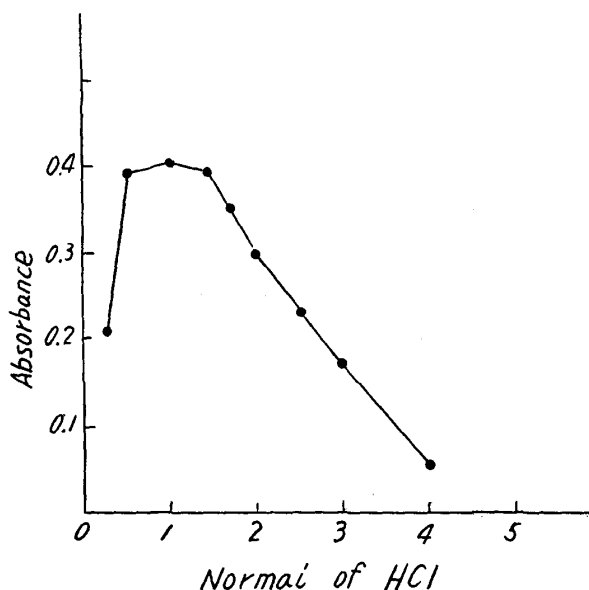
Fig. 2. Relation between absorbance and acidity

were nearly constant in this acid region. The molecular absorption coefficient at 580 mμ in 1 Nhydrochloric acid was 9.5×10^3, and this color complex was stable for about 1 hour after extraction.

IV. Preparation of calibration curve

Various amounts form 10 to 100 μg of tin were taken from tin standard solution and put in separatory funnels, and made up to 20 ml in 1 N hydrochloric acid.

The extraction solution of 10 ml was added to each funnel and shaken for a few minutes. After settling, the aqueous layer was discarded and the organic layer was put in a cell.

The absorbance of the organic solution was measured at the wave length of 580 mμ against the blank solution prepared as described above in the absence of tin. These results are shown in Fig. 3A, giving the applicability of Beer's law for the relation between the absorbance and the stannic ion below 100 μg. Alternatively, the organic layer was washed with 20 ml of 1 N hydrochloric acid to discard the excess reagent as possible. Then, this solution was transferred to the volumetric flask of 10 ml and diluted to 10 ml with ethyl acetate. Through this procedure the value of blank test was decreased and the calibration curve B was obtained. In this case, the fluctuation of the absorbance was less than the case of calibration curve A, but the absorbance was decreased as it was finally diluted with ethyl acetate to 10 ml. As cyclohexanone has more solubility in water, the organic layer decreased to six or seven tenth of the original volume by one extraction, and the absorbance increased. Then the procedure had good reproducibility with little variation. Therefore, this procedure was adopted for the analysis of real samples.

V. Interference ions

The interference elements in the proposed reaction were investigated. Various amounts of metal ions were added to 50 μg of tin, and treated by the procedure of the preparation of calibration curve. In addition to these studies, the tolerance limit range of the diverse elements in the presence of 2.0 ml of per cent tartaric acid and 3.0 ml of 3 per cent EDTA. These results are shown in Table 1.

Table 1. Limit amount of coexisting metal ions for the
determination of 50 μg of Sn.

Diverse ion	Coexisting limit		
	Without masking reagent	2.0 ml tartaric acid sol. present	3.0 ml EDTA sol. present
Fe^{3+}	< 0.20mg	< 0.20mg	< 0.20mg
Cu^{2+}	< 0.20mg	—	<11.0mg
Sb^{3+}	—	<11.0mg	<15.0mg
Sb^{5+}	< 2.2 mg	< 8.2mg	—
As^{3+}	<10.0mg	<15.0mg	<15.0mg
Bi^{3+}	< 8.0mg	<10.0mg	<15.0mg
Mo^{6+}	< 5.0μg	< 5.0μg	< 5.0μg
V^{5+}	<20.0μg	< 0.20mg	<20.μg
Pb^{2+}	< 0.27mg	—	—
Mn^{2+}	~88.0mg	—	—
Zn^{2+}	~120.0mg	—	—

From these results, it was seen that the most unfavorable ions were molybdate, vanadate, ferric and cupric ions, and so it was necessary to separate them if they were accompanied. 50 per cent tartaric acid up to 5.0 ml, 50 per cent ammonium citrate solution up to 2.0 ml and sulfuric acid less than 1 N did not interfere with this reaction.

VI. Determination of tin in steel

Prior to the application of this method for the determination of tin in steel, manganese dioxide method, thiosulfate method and hydrogen disulfide method were investigated to separate tin from iron. A little coprecipitation of iron was found in manganese dioxide method and the separation by thiosulfate had some difficulty, so that the hydrogen sulfide method was utilized.

1. Analytical procedure

2~5 g of samples is dissolved in 20ml of hydrochloric acid (1+1) and 5ml of nitric acid, and then the solution is boiled to expel oxides of nitrogen. After cooling, the solution is nearly neutralized with ammonium hydroxide and boiled for a few minutes. 5 ml of hydrochloric acid is added to the solution and diluted with warm water to 300 ml. Hydrogen sulfide is bubbled for about 20 minntes in the solution to precipitate tin as sulfide. After the filtration, the precipitate is washed a few times with warm water saturated with hydrogen sulfide and with warm water. The precipitate is transferred to a beaker together with filter paper and dissolved in 5 ml of sulfuric acid and 10 ml of nitric acid by fuming. The decomposition of the filter paper can be completed by the addition of a suitable
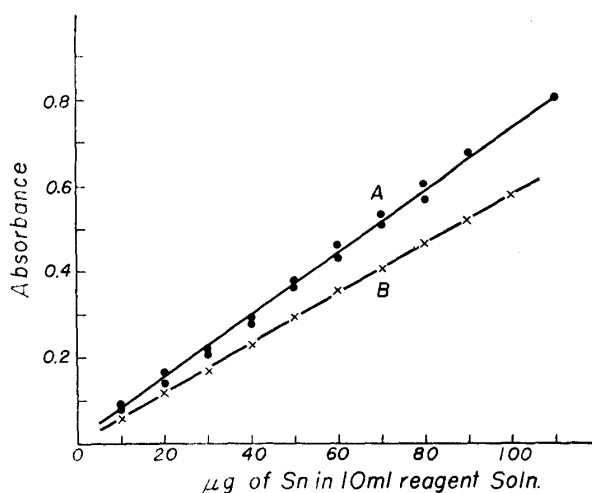
Fig. 3. Calibration curve

amount of nitric acid. After the fuming of sulfuric acid, the salt is dissolved in 1N hydrochloric acid and diluted to 100 ml with 1 N hydrochloric acid in the volumetric flask of 100 ml. 10 ml of the sample solution is transferred to a separatory funnel, and 10 ml of 1 N hydrochloric acid, 20 ml of 50 per cent tartaric acid, 2 ml of 3 per cent EDTA solution and 10 ml of extraction solution are added, and shaken for a few minutes. After settling for a few minutes, the aqueous layer is discarded, and 1 N hydrochloric acid of 20 ml is added. Again the solution is shaken and mixed to remove the excess of alizarin blue. After a few minutes

Table 2. Determination of Sn in steels and cast irons.

Sample	Sample taken (g)	Sn found (μ)	Sn (%)	Other method (%)
Steel 1	0.9936 0.9995	33.5 36.2	0.034 0.036	0.033 v
Steel 2 (Cu: 0.19%)	2.0034 1.9976	65.0 62.0	0.032 0.032	0.031 v
Steel 3 (Cu: 0.20%)	0.9992	31.5	0.031	0.033 c
Steel 4	1.0009	4.5	0.0005	0.001 c
Cast iron 1	1.9923 1.9940	19.5 19.0	0.0096 0.0095	0.013 c
Cast iron 2	2.0007 1.9963	17.6 17.6	0.0088 0.0089	0.010 c

v: volumetric method; c: cacotheline method

standing, the aqueous layer is discarded and the organic phase is transferred to dried volumetric flask. The extracted solution is diluted with ethyl acetate to 10 ml, and the absorbance of this solution is measured at 580 mμ against the blank solution treated with reagents as above.

The calibration curve is made by the same treatment of the solution containing the known amount of tin with electrolytic iron (cf. Fig. 3B).

2. Analytical results

The results of application of this method to some actual sample are shown in Table 2. These analytical values had good agreements with the results obtained by cacotheline method or by volumetric method.

VII. Determination of tin in copper, lead, zinc or their alloys

A small amount of tin in copper, lead, zinc or in their alloys was determined after it had been separated from matrix by the manganese dioxide method.

1. Analytical procedure

2~5 g of sample is dissolved in 20 ml of nitric acid (1+1) and boiled. 5 ml of manganese sulfate (5 per cent) is added to this solution and diluted with water to about 200 ml. The precipitate of manganese dioxide is formed by addition of 3 ml of potassium permanganate solution (3 per ent) and boiling for a few minutes. The precipitate of manganese dioxide is filtered and washed a few times with hot water and transferred to the original beaker as much as possible. The precipitate on the filter paper is dissolved in beaker through the filter paper with a mixture of 10 ml of nitric acid (1+1) and a small amount of hydrogen peroxide. The filter paper is washed with hot water, and washing solution is combined with the filtrate.

The solution is boiled to decompose hydrogen peroxide, and diluted to about 100 ml with hot water. After boiling, tin is coprecipitated with manganese dioxide as described above, and the precipitate is filtered and washed.

The precipitate is transferred to the original beaker as much as possible. The precipitate remaining on the filter paper is dissolved in 10 ml of nitric acid (1+1) and a small amount of hydrogen peroxide, and the acid solution is received through the filter paper, and the filter paper is washed with hot water. The washing solution is combined with the filtrate. This solution is boiled to decompose hydrogen peroxide and evaporated to fume with 5 ml of sulfuric acid. After fuming of sulfuric acid, the solution is cooled and diluted to 100 ml with 1 N hydrochloric acid. Following the previous procedure, tin is extracted and analyzed with the same procedure as that in the determination of tin in steel.

In the case of zinc metal, the double precipitation is not necessary because of small interference of zinc.

2. Analytical results

The analytical results of tin in copper-tin alloys, lead and zinc are shown in Table 3. As shown in this table, in the case of nonferrous metal, tin of 0.001~ 0.1 per cent could be determined after the manganese dioxide separation.

Summary

1. The determination of tin was investigated with alizarin blue.

2. The stannic ion was extracted with alizarin blue-cyclohexanone-ethyl

Table 3. Determination of Sn in Cu alloy, Zn and Pb.

Sample	Sample taken (g)	Sn added (μg)	Sn found (μg)	Sn reproduced (μg)	Sn (%)	Cacotheline method (%)
Cu-alloy 1	1.9992 1.6900	— —	36.3 30.5	— —	0.0182 0.0178	0.0180
Cu-alloy 2	0.9975 1.9990	— —	29.2 59.4	— —	0.0293 0.0298	0.033
Pb 1	1.0996 1.0996 1.0996	0.0 50.0 90.0	2.0 53.4 90.0	— 51.4 88.0	0.0018 — —	— — —
Pb 2	0.8670 0.8670 0.8670	0.0 50.0 90.0	9.5 59.3 98.5	— 49.8 89.0	0.011 — —	— — —
Zn 1	2.9362 2.9362 2.9362	0.0 50.0 90.0	1.0 53.0 91.0	— 52.0 90.0	0.0003 — —	— — —
Zn 2	0.3675	—	36.5	—	0.0993	—
Zn 3	0.1486	—	53.5	—	0.360	—
Zn 4	0.9170	—	14.5	—	0.0158	—

acetate extraction solution from 1N hydrochloric acid.

The maximum absorption wave length of this solution was 580 mμ, and the absorbance was obeyed to Beer's law for the tin below 100 μg per 10 ml.

3. Molybdate ion seriously interfered with this reaction. The interferences of ferric ion and vanadate ion were removed by the hydrogen sulfide separation. The effects of antimony and bismuth were avoided by the presence of tartaric acid and EDTA.

4. By using this reaction, 0.001~0.1 per cent of tin in iron, steel and non-ferrous alloys could be determined with good agreement with the values obtained by other methods.

Acknowledgement