A New Method of Spectrophotometric Determination of Zinc with Alizarin Blue : Application to Estimation of Zinc in Tin and Lead

A New Method of Spectrophotometric Determination of Zinc with Alizarin Blue. Application to Estimation of Zinc in Tin and Lead*

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Synopsis

Alizarin blue combining with zinc formed a colored complex at pH 5.6, and was extracted from aqueous phase by using a mixture of cyclohexanone and ethyl acetate. This complex had a maximum absorption at 635 mμ, the molecular absorption coefficient being 2.69×10^4. After the interference of several cations and anions were examined, microquantities of zinc in tin and lead were successfully determined by this method.

I. Introduction

Oxine method[1], dithizone method[2] and several others have been applied to the determination of small amount of zinc. It is, however, difficult to analyze zinc below 0.01 per cent by the oxine method. By the extraction of oxinate with methyl isobutyl ketone or with other solvents, zinc has not been estimated with sufficient sensitivity. Although the dithizone method has very high sensitivity in the spectrophotometric analysis, the presence of a small amount of copper, lead and other heavy metals interferes with it. Unless redistilled water and purified reagents are used, this method is practically difficult to apply to the microdetermination of metallic ions.

So, the present author aimed at the utilization of alizarin blue[3] as the spectrophotometric reagent of zinc, and a new analytical procedure for zinc was attained, which was applicable to the determination of zinc in certain kinds of metal.

II. Reagnets and apparatus

1. Reagents

(i) Alizarin blue-cyclohexanone extraction solution

Alizarin blue dissolves not in benzene, alcohol, carbon tetrachloride, or amyl acetate, but in pyridine, cyclohexanone, tetrahydrofrane or in dioxane. From the

* The 1046th report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the Journal of the Japan Institute of Metals, **23** (1959), 698.

(1) H. Gotô, J. Chem. Soc. Japan, **54** (1933), 725 et al.

(2) E.B. Sandell, *Colorimetric Determination of Traces of Metals* (1950), 619.

(3) F. Feigel and A. Calelas, Anal. Chim. Acta, **8** (1953), 339.

investigation on the solubility of zinc-alizarin blue complex in organic solvents, it was found that the mixed solvent of cyclohexanone and iso-propylether or of cyclohexanone and ethyl acetate was optimum for the extraction solution. Then, the solution for extraction was prepared as follows. After 0.100 g of alizarin blue was dissolved in 500 ml cyclohexanone, 500 ml of ethyl acetate was added and mixed well. This solution was used as the extraction solution.

(ii) Potassium cyanide, sodium thiosulfate, ammonium fluoride, acetic acid and sodium acetate used were all of analytical grade.

(iii) Zinc standard solution

0.2 g zinc metal was exactly weighed and dissolved with hydrochloric acid. This solution was diluted to 250 ml with distilled water and stocked as a standard solution.

2. Apparatus

Hitachi spectrophotometer of the type EPU-2 with 1 cm cells and pH meter made by Toa Dempa were used.

III. Reaction of alizarin blue with zinc or other metals

The extractivity and the reactivity of various metal ions with a mixed solution of alizarin blue-cyclohexanone-ethyl acetate were examined.

In Table 1 suitable pH for the extraction of metal ions and maximum absorption wave length of their metal complexes are shown. In this case, the higher range of pH was controlled by acetic acid and sodium acetate buffer solution.

The absorption curve for zinc complex and the relation between the absorbance and pH of the aqueous solution are shown in Figs. 1 and 2, respectively. The procedure was as follows: The standard solution containing 9.0 μg zinc was put into a separatory funnel to which 20 ml of acetic acid and sodium acetate buffer

Table 1. Suitable pH of some metal ions for the extraction and reaction with alizarin blue, and wave length of maximum absorption and molecular absorption coefficient of their complex.

Ion	Extraction & reaction pH	Wave length of maximum absorption (m, μ)	Molecular absorption coefficient
Zn^{++}	5.5～7.0	635	2.79×10^4 at pH:5.6
Al^{+++}	6.5～7.5	600	1.10×10^4 at pH:6.5
Mn^{++}	6.4～7	640	1.45×10^4 at pH:6.4
Cd^{++}	5.5～7	650	2.63×10^4 at pH:5.6
Ni^{++}	6.0～7	650	2.54×10^4 at pH:6.0
Sn^{4+}	0.5～2N-HCl	580	0.95×10^4 at 1N-HCl
Mo^{6+}	0.1～4N-HCl	560	1.06×10^4 at 1N-HCl
W^{6+}	0.1～3N-HCl	545	0.20×10^4 at 1N-HCl
Fe^{+++}	pH<0.2N-AcOH	ppt	—
Cu^{++}	pH<0.5N-AcOH	ppt	—
Co^{++}	3.6～	ppt	—
Pb^{++}	3.6～	ppt	—
Ag^{+}	3.6～	ppt	—
Hg^{++}, Ti^{4+}, Ce^{4+}	～7～	react	—

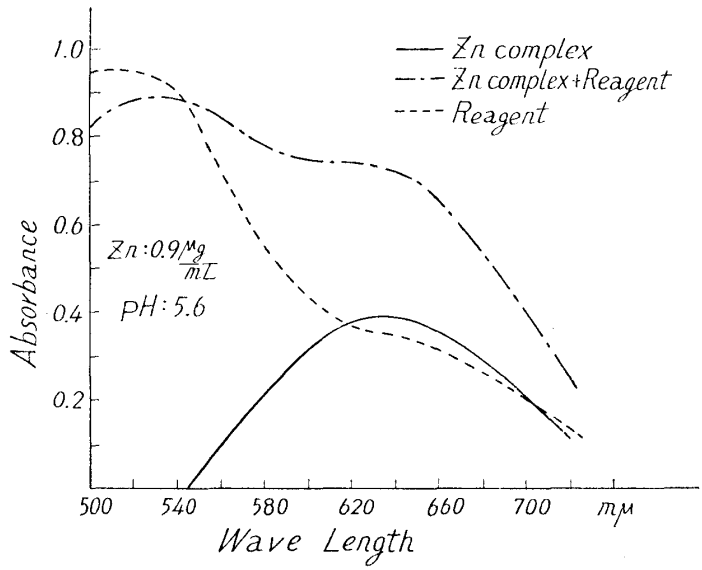

Fig. 1. Absorption curve

solution were added. After the dropping of 10 ml of extraction solution into the separatory funnel exactly, the solution was shaken well for a few minutes. A portion of the organic phase was transferred to a cell and its absorbance was measured against the blank solution which treated without zinc as above. The relation between the amount of zinc and its absorbance at pH of 5.6 and at the wave length of 365 mμ was obtained as shown in Fig. 3. From this figure it will be seen that the absorbance of the zinc compound is obeyed to Beer's law up to the concentration of 20μg /ml of zinc.

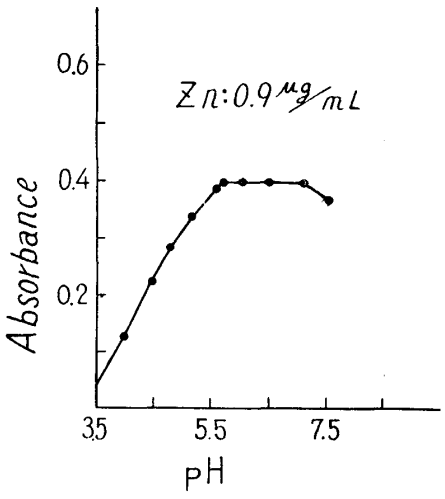

Fig. 2. Relation between absorbance and extraction pH.

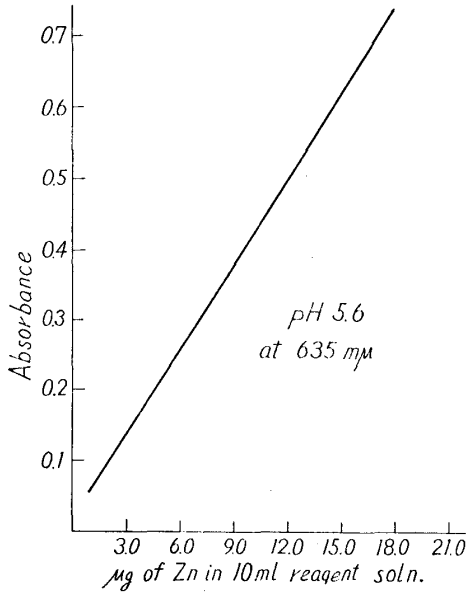

Fig. 3. Calibration curve

IV. Influence of masking reagent on the extraction of zinc

1. The influences of potassium cyanide, EDTA and sodium citrate on the extraction of zinc

The influences of potassium cyanide, EDTA and sodium citrate on the extraction of zinc, being used as the masking reagents in the case of dithizone extraction, were examined.

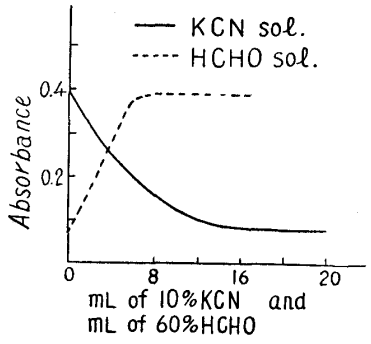

Fig. 4. Influence of KCN and HCHO on the extraction of Zn

9 μg of zinc was taken into a separatory funnel, 10 per cent potassium cyanide solution with pH 5.6 was added as shown in Fig. 4, and acetic acid-sodium acetate buffer solution of pH 5.6 was added to it. After the solution had been made up to about 20 ml, 10 ml extraction solvent was added, and shaken for a few minutes. The solution was then treated as in the case of the preparation of calibration curve in Fig. 3. These results are shown in Fig. 4. From this result, zinc was masked by about 15 ml of potassium cyanide (10 per cent). To the masked zinc with 20 ml potassium cyanide solution (10 per cent), various volume of the formalin solution (60 per cent), pH of which was controlled at 5.6, was added as shown in Fig. 4, and zinc in this solution was extracted. From this figure, it will be seen that almost masked zinc with 20 ml potassium cyanide (10 per cent) is demasked by about 8 ml of formalin solution (60 per cent).

Next, the influence of 5ml of sodium citrate (50 per cent) solution on the extraction of zinc was examined. The amount of zinc extracted from this solution was less than one sixth of the present case, so the influence of citrate ion was found.

2. The influences of sodium thiosulfate and ammonium fluoride on the extraction of zinc

The influence of sodium thiosulfate, being used for masking copper, cadmium and lead, on the extraction of zinc was examined. 3 ml of sodium thiosulfate (50 per cent) was added to the various amounts of zinc, and zinc was extracted at pH 5.6. The results are shown in Table 2, and it was found that the presence of sodium thiosulfate had no influence on the extraction of zinc. Further, the influence of cadmium on the extraction of zinc in the presence of 3 ml of thiosulfate solution

Table 2. Influence of $Na_2S_2O_3$ on the extraction of Zn (at pH: 5.6, 3 ml of $Na_2S_2O_3$ (50%) was added).

Zn taken (μg)	3.6	6.0	12.0	18.0
Zn found (μg)	3.6 3.8	6.1 5.8	11.8 11.7	18.1 17.8

(50 per cent) was studied. These results are shown in Table 3; about 0.5 mg of cadmium was permissible to exist without any effect on the extraction of zinc. Similarly, the influences of lead and copper which must form precipitate combining with the reaction of alizarin blue, were examined. These metals were allowed to be present up to 0.4 mg with zinc.

Table 3. Influence of Cd on the extraction of Zn in the presence of $Na_2S_2O_3$.

Cd added (mg)	Zn used (μg)	Zn found (μg)	
0.00	9.0	9.1	9.3
0.10	9.0	8.9	9.2
0.248	9.0	9.2	9.0
0.494	9.0	9.3	8.9
0.988	9.0	9.4	9.8

Table 4. Influence of NH_4F on the extraction of Zn.

Zn taken (μg)		6.0	12.0	18.0
Zn found (μg)	Without Fe	6.0 6.1	12.0 11.7	18.2 17.9
	1 mg of Fe was added	6.2 6.2	12.1 11.8	18.4 17.9

Then, the effect of ammonium fluoride which has been used as the masking reagent for iron was studied. The results in Table 4 were obtained by the addition of 5 ml ammonium fluoride (20 per cent). The presence of 5 ml ammonium fluoride (20 per cent) could avoid the interference of 1 mg iron without any disturbance of the extraction of zinc. From these results, the procedure of the determination of zinc in lead and tin could be established.

V. Determination of zinc in lead and tin

1. Determination of zinc in lead

After lead had been separated as lead sulfate, zinc in lead was determined as follows:

Analytical procedure:

1.0～3.0 g sample is dissolved in 20 ml of nitric acid (1+4). After 4 ml of sulfuric acid is added, solution is evaporated to fume, and cooled. 30 ml of water is added and the precipitate of lead sulfate is filtered off. The precipitate is washed with about 10 ml of sulfuric acid (3+97). The filtrate and washing water are combined with each other, and pH of the solution is controlled at 5.5 with ammonium

hydroxide and 2N-sodium acetate. Then the solution is transferred to the volumetric flask of 100 ml, and diluted to the mark with water. The aliquote volume of this solution containing zinc less than 20 mg is taken into a separatory funnel. 20 ml of acetic acid-sodium acetate buffer solution, 5 ml of sodium thiosulfate (50 per cent) and 2 ml of ammonium fluoride (20 per cent) are added, and mixed well. 10 ml of extraction solution is added, and zinc is extracted with this solution. After settling the solution for a few minutes, the absorbance of the extraction solution is measured at 635 mμ against the blank solution treated by the aqueous solution with the same composition as the sample except zinc. Zinc in the extraction solution is then determined from the calibration curve obtaimed by the known amount of zinc solution.

In the case of the preparation of calibration curve, each amount of zinc is added to lead nitrate with the weight from 1.85 to 5.55 g or lead metal from 1 to 3 g, and treated as the above procedure (cf. Fig. 3). When the sample contains tin or antimony, the solution is evaporated to fume of sulfuric acid after the disolution of the sample with nitric acid, and the addition of 2 to 3 ml of bromine and from 10 to 20 ml of hydrobromic acid.

2. Determination of zinc in tin

The amount of zinc in tin is analyzed after the matrix is evaporated by the treatment with bromine and hydrobromic acid.

Analytical procedure:

Sample of 1.0 to 3.0 g is taken in the beaker, to which are added 18 ml of hydrobromic acid and 2 ml of bromine. The solution is heated and evaporated to substantial dryness. 5 ml of hydrobromic acid and bromine (9: 1) are added again, and heated to substantial dryness. After cooling, 5 ml of 2N acetic acid is added. The wall of beaker is rinsed with water, and the solution is boiled. After cooling, the solution is transferred to 100 ml volumetric flask. The washing solution of the wall of beaker is mixed with the solution in the flask. 45 ml of 2N sodium acetate solution is added to the solution, which is diluted with water to 100 ml. The solution is mixed well, and an aliquote volume of this solution containing less than 20μg of zinc is taken into a separatory funnel. 20 ml of acetic acid-sodium acetate buffer solution (pH 5.6), 50 ml of sodium thiosulfate solution (50 per cent) and 2 ml of ammonium fluoride solution (20 per cent) are added and mixed very well. The extraction solution of 10 ml is added and then the procedure as described in the determination of zinc in lead is used. The calibration curve is prepared by the same procedure after the various amounts of zinc are added to tin of 1 to 3 g.

3. Analytical results

By the procedure of V–1 and V–2, lead and tin metal were analyzed. The results are shown in Table 5. From these results, it was concluded that zinc of 0.0001 to 0.01 per cent in tin and lead was determined by the proposed simple procedure.

Table 5. Determination of Zn in Pb and Sn.

Sample	Sample taken (g)	Zn added (μg)	Zn found (μg)	Zn reproduced (μg)	Zn (%)
Pb(A)	0.1390	0.0	2.6	—	0.0018
		5.8	8.5	5.9	—
		11.6	14.0	11.4	—
Pb(B)	0.2009	0.0	0.7	—	0.00035
		5.8	6.7	6.0	—
		11.6	12.8	12.2	—
Pb(C)	0.1962	0.0	9.1	—	0.00046
		5.8	14.9	5.8	—
		11.6	19.9	10.8	—
Sn(A)	0.2210	0.0	1.7	—	0.00077
		5.5	7.1	5.4	—
		11.0	13.7	11.0	—
Sn(B)	0.2072	0.0	1.2	—	0.00058
		5.5	6.5	5.3	—
		11.0	13.0	11.8	—
Sn(C)	0.2587	0.0	0.4	—	0.00014
		5.5	6.2	5.8	—
		11.0	12.1	11.7	—

Summary

(1) A new spectrophotometric determination of zinc with alizarin blue was examined.

(2) The extraction condition of zinc complex, and the reaction condition of copper, cadmium and other metals with alizarin blue were exmained.

(3) The effect of some masking reagents on the extraction of zinc complex was exmained.

(4) These results were applied to the determination of zinc in lead and tin and satisfactory results were obtained.

Acknowledgement

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