Determination of Small Amounts of Copper and Iron with X-Ray Fluorescent Spectroscopy. Combination with Organometallic Precipitation

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The determination by X-ray fluorescent spectroscopy[1] of small amounts of copper and iron in metals without separation is difficult. Therefore, the application of organometallic precipitation to X-ray fluorescent spectroscopy has been investigated. In previous determinations of small amounts of metals by X-ray fluorescent spectroscopy, the element to be analyzed has been concentrated on filter paper or on Mylar film or metal foils[2]. The organic precipitate of metals without carriers[3], however, has not been used as a sample for X-ray spectroscopy.

On the other hand, it has been recognized that alizarin blue reacts with copper and iron[4] in acidic solutions. Investigation was therefore carried out, first, to find the optimum conditions for the reaction of alizarin blue with copper and iron and then X-ray fluorescent spectroscopy, combined with this organic precipitation separation, was applied to the determination of small amounts of copper and iron.

Experimental and Results

Reagents.—*Alizarin Blue Solution.*—Alizarin blue-saturated solution in tetrahydrofran was used.

Standard Solution of Copper.—Copper (0.4∼0.5 g.) was dissolved with nitric acid, and a solution containing 5∼100 μg. of copper was prepared by dilution with water when needed. A standard solution of iron was also prepared, as well as a copper standard solution. The nitric acid, hydrochloric acid and sulfuric acid used were all analytical grade reagents. A 0.2 M EDTA solution, a 0.1 M glycine solution and a 20% potassium thiocyanate solution were also used in the experiment.

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[1] K. Hirokawa, *J. Japan Inst. Metal* (*Nippon Kinzoku Gakkaishi*), **24**, 555 (1960).

[2] H. G. Pfiffer, *Nature*, **174**, 397 (1954); R. C. Hirt *Anal. Chem.*, **28**, 1649 (1956); J. F. Fagel, ibid., **29**, 1287 (1957).

[3] J. E. Fagel et al., ibid., **29**, 1287 (1957).

[4] K. Hirokawa, *J. Japan Inst. Metal* (*Nippon Kinzoku Gakkaishi*), **23**, 698 (1959); F. Feigl et al., *Anal. Chim. Acta*, **8**, 339 (1953).

Instruments. — G. E. XRD-5 X-ray spectrometer with AEG50-S tungsten tube, lithium fluoride analyzer, 0.025 cm. solar slit, and 2 SPG detector, was used. The X-ray irradiation area was controlled by the aluminum plate with a round window 1.5 cm. in diameter. A Hitachi spectrophotometer, model EPU-2, with 1 cm. cells was also used.

Condition of Precipitation. — The formation of alizarin blue precipitate with copper or iron in an acid solution has been already reported[4]. In order to determine the optimum conditions for the precipitation, the following experiments were carried out.

From the copper standard solution, 40.4 μg. of copper was placed in a beaker. The acidity of this solution was controlled with hydrochloric acid and ahydr ochloric acid-glycine buffer solution, and the total volume was made up to about 50 ml. After 10 ml. of the alizarin blue solution* had been added, the rest was left to stand for a few minutes; the precipitates formed were then filtered and washed with water a few times. The precipitate and filter paper were together transferred back into the original beaker, and the precipitate was completely decomposed by heating with 5 ml. of sulfuric acid and 10 ml. of nitric acid. After the fuming of the sulfuric acid, the deposited salt was dissolved with 20 ml. of nitric acid (1+2) and cooled. This solution was diluted with water to 100 ml., one-fifth of this solution was taken into a separatory funnel; then the amount of copper in it was determined by the diethyl dithiocarbamate method. From these results, the relation between the pH of the solution and the content of copper in the precipitate was determined, as shown in Fig. 1; it was discovered that the copper was completely precipitated above a pH of 0.7. Next, the same attempt was carried out for the precipitation at a more acidic range in the presence of 2 ml. of 0.2% potassium thiocyanate, but the presence of potassium thiocyanate did not affect the precipitation. Similarly, 282 μg. of iron was treated with the same procedure as has been previously described. The precipitation of iron with alizarin blue was decomposed, and the amount of iron was determined by the spectrophotometric method using potassium thiocyanate. The relation between precipitation and pH is shown in Fig. 2. In this case, the presence of potassium thiocyatate had no effect on the precipitation of iron. From these results, it was recognized that copper and iron was completely precipitated with alizarin blue at pH values above 1.0.

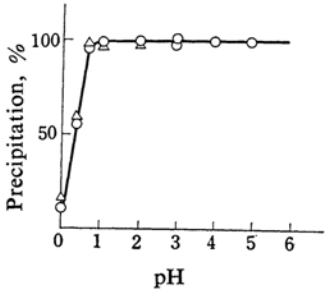

Fig. 1. The precipitation of Cu at various pH.

—○— KSCN not present
—△— KSCN present

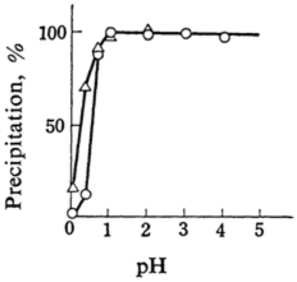

Fig. 2. The precipitation of Fe at various pH.

—○— KSCN not present
—△— KSCN present

Precipitation of Calibration Curves of Copper and Iron, and their Interaction.—As has been reported in the previous paragraph, copper and iron were completely precipitated with alizarin blue at pH values above 1; calibration curves for the X-ray spectroscopy of copper and iron can, therefore, be prepared with the following procedure. Copper (20∼100 μg.) were taken into a beaker and made up to 50 ml. of a 0.02∼0.1 N hydrochloric acid solution. Ten milliliters of alizarin blue solution was added to it, forming the precipitate. After being left standing for a few minutes, the precipitate was filtered with the apparatus as shown in Fig. 3. The precipitate on the filter paper was washed a few times with water and stuck with cellophane tape to the filter paper. Iron (20∼100 μg.) was treated the same way as the copper. These samples were put in the sample holder and baked with aluminum plate. The fluorescent X-ray intensity of each element in these samples was measured under the conditions shown in Table I. The results are shown in Fig. 4 for copper and in

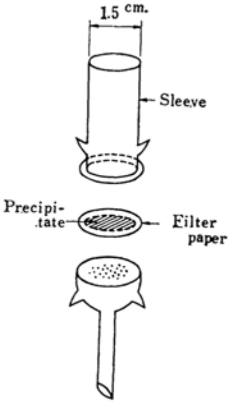

Fig. 3. Schematic diagram of filter.

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* Five milliliters of the alizarin blue solution was enough to from the precipitate with about 400 μg. of copper; 10 ml. of the alizarin blue solution was used throughout the experiments.

Fig. 5 for iron. Below 100 μg. of iron or copper, the X-ray intensity is proportional to the amounts of the element in the samples. Using these calibration curves, the effect of iron on copper and of copper on iron could be investigated. The results obtained appear in Tables II and III. The possibility of a simultaneous determination of copper and iron under the same conditions was also recognized. Therefore, this method was applied to the determination of copper and iron in some metals.

TABLE I. OPERATION CONDITIONS FOR THE DETERMINATION OF Cu AND Fe

Excitation soure	40 kV. 15 mA.
Spectral lines (Å)	CuK_α (1.542 Å) 45.02°
LiF$_{2\theta°}$	FeK_α (1.937 Å) 57.50°
Fixed counting	10000 counts
Irradiated area	1.5 cm. in diameter

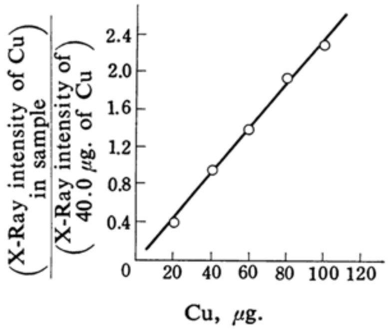

Fig. 4. Calibration curve for Cu.

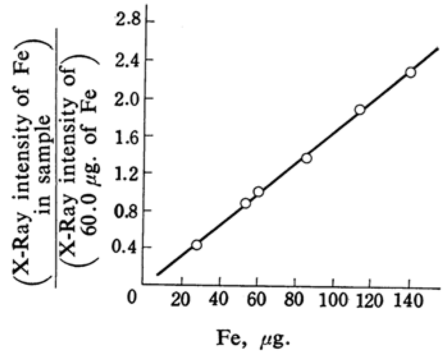

Fig. 5. Calibration curve for Fe.

Simultaneous Determination of Copper and Iron in Nonferrous Metals.—Using the system of measurement described above the determination of coppr and iron in nonferrous metals was undertaken. The nonferrous metals used were aluminum, zinc, manganese and nickel, which do not react with alizarin blue at pH values below 5; the analytical procedure used was as follows.

Procedure. — A definite sample (0.5∼1.0 g.) was taken and dissolved with 5∼10 ml. of hydrochloric acid or nitric acid, and the sample solution was prepared as a 0.02∼0.1 N acid solution of 100 ml. From this solution a one-tenth or one-twentieth solution (containing below about 100 μg. of copper and iron) was taken out, and an alizarin blue solution was added. In accordance with the procedure for the preparation of the calibration curve previously described, copper and iron were analyzed. These results are shown in Table IV. On the basis of these results, small amounts of copper and iron in these metals can be rapidly analyzed with a simple procedure.

TABLE II. THE INFLUENCE OF Fe ON THE DETERMINATION OF 40.4 μg. OF Cu

Fe used μg.	Cu found μg.	Difference μg.
56.4	41.0	+0.6
112.8	40.4	0.0
225.6	40.0	−0.4

TABLE III. THE INFLUENCE OF Cu ON THE DETERMINATION OF 56.4 μg. OF Fe

Cu used μg.	Fe found μg.	Difference μg.
40.4	57.2	+0.8
80.8	57.3	+0.9
161.6	56.4	0.0

TABLE IV. DETERMINATION OF Cu AND Fe IN Al, Zn, Mn AND Ni

Sample	Sample taken g.	Cu added μg.	Cu found μg.	Cu recovered μg.	Fe added μg.	Fe found μg.	Fe recovered μg.
Al	0.044	0.0	0.9	—	0.0	1.5	—
	0.089	0.0	2.0	—	0.0	3.2	—
	0.089	41.8	44.0	42.0	41.8	44.0	40.8
Zn	0.057	—	—	—	0.0	4.2	—
	0.114	0.0	2.2	—	0.0	8.5	—
	0.114	38.3	40.8	38.6	—	—	—
Mn	0.052	0.0	1.2	—	0.0	0.5	—
	0.104	0.0	2.3	—	0.0	0.5	—
	0.104	—	—	—	56.5	55.5	55.5
Ni	0.041	0.0	4.9	—	0.0	3.8	—
	0.041	38.3	42.8	37.9	—	—	—
	0.082	0.0	9.0	—	0.0	8.0	—
	0.082	38.3	47.0	38.0	—	—	—

Discussion

The simultaneous determination of copper and iron in aluminum, zinc, manganese or nickel has been investigated. Copper in zinc, iron in manganese, or copper in nickel is difficult to analyze with a non-destructive method due to the high background of the matrix. Therefore, it is necessary to diminish this matrix effect as much as possible. Examples of spectrograms of iron in manganese, of copper in nickel and of zinc after separation are indicated in Fig. 6; these excitation conditions are similar to those in Table I. In the case of manganese and zinc, the separation was complete, but in the case of nickel, a small amount of it remained. However, as indicated in Table IV, the remaining nickel had little effects on the copper and iron. On the basis of these facts, it was considered that the presence of organic materials decreases the effect of diverse metals, and hence, that the effect of nickel is negligibly small for the X-ray spectroscopic determination of copper. Iron, nickel and copper also exhibited similar behavior regarding X-ray intensity, so the presence of a small amount of nickel has no effect if the total amount of copper and nickel is below three times that of iron.

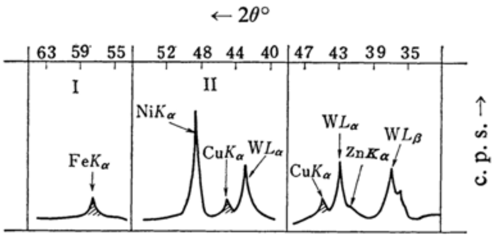

Fig. 6. Examples of spectrograms of Fe in Mn (I), and Cu in Ni (II) and Zn (III) after separation.

I 0.104 g. of Mn was taken, and full scale of the chart was 100 c. p. s.
II 0.082 g. of Ni was taken, and full scale of the chart was 500 c. p. s.
III 0.114 g. of Zn was taken, and full scale of the chart was 500 c. p. s.

Adding these findings to the results of the previous experiments, oxine and other organic reagents may be used for concentration of a small amounts of an element for purposes of fluorescent X-ray spectroscopy. Alizarin blue has the advantages that the precipitation reaction takes place at low pH regions and that it can be treated with a simple procedure. The amounts of silver and molybdenum, which react with alizarin blue under the same conditions[4)], can be determined as well as those of copper and iron.

Summary

The simultaneous determination of small amounts of copper and iron with X-ray fluorescent spectroscopy combined with organic precipitation was investigated. Using an alizarin blue solution, which reacts with copper and iron at a low pH value, as the precipitant, satisfactory results were obtained. The amounts of copper and iron in aluminum, zinc, manganese and nickel were rapidly determined with X-ray fluorescent spectroscopy after this separation.

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