Extraction-Spectrophotometric Determination of Average Valence of Copper in Superconductor Y-Ba-Cu-O

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(Received October 24, 1991)

The determination method of the average valence of copper in a Y–Ba–Cu–O superconductor has been investigated. Spectrophotometry was introduced to the iodometry considered to be a conventional method in order to decrease the amount of sample used. The iodine liberated by the reaction between Cu^{2+} and/or Cu^{3+} and I^- ions was extracted into chloroform with Zephiramine ($Zeph^+Cl^-$) as a $Zeph^+I_3^-$ ion pair complex. The extraction of I_3^- enhanced the reproducibility. The effect of the HCl concentration was significant. The sample was dissolved with 5 ml of a 0.1 M ($M=mol\,dm^{-3}$) HCl solution by means of ultrasonic irradiation. The employed method decreased the amount of consumed sample down to 4 mg. The modified method, using cuproine, decreased the amount down to 2 mg.

The average valence of copper in high-T_c oxide superconductors is closely related to the properties of superconductor.[1,2] Therefore, many methods for the determination of the valence states of copper have been reported: i.e., iodometry (titration),[3] gravimetry,[4] gas chromatography,[5] coulometric titration,[6] and XPS.[7] These methods, however, consume large amounts of the samples. Superconductor samples are very valuable due to the fact that their preparation conditions, such as the temperature, gas, and rate of cooling from high temperature, must be strictly controlled. A long time is required in order to prepare favorable samples. By using small samples, the determination of copper valences is very important for a film superconductor. Iodometry has commonly been used to determine the amount of Cu^{2+} and Cu^{3+} in a superconductor by using a large amount of the sample.[8] Iodometry is superior to other methods, which include the XPS method,[7] in terms of both accuracy and precision. In this paper, the solvent-extraction of iodine is discussed regarding the iodine liberated by a reaction between Cu^{2+} and/or Cu^{3+}, as well as I^- ions. The decrease in the amount of consumed sample could be anticipated by introducing extraction-spectrophotometry to iodometry.

Experimental

Apparatus and Reagents. A Shimadzu Model UV-2100S spectrophotometer was used for the absorbance measurements. An Iwaki KM shaker (350 rpm) was used for extraction. An A and D model ER-182A semi-micro balance, which is available above the range of 0.01 mg, was used for weighing the samples and copper sulfate. Zephiramine ($Zeph^+$ Cl^-, Wako Chemical Co.) was used as a 0.04% aqueous solution. Copper sulfate pentahydrate, pottasium iodide, and the other reagents used were of analytical grade.

Procedure. The standard procedures were as follows; 5 ml of a 0.1 M HCl solution and 1 g of KI were taken into a 50 ml volumetric flask. Then, 2—3 mg of the sample weighed exactly (three significant figures) was added to the volumetric flask. After the sample solution was placed for 10 min in an ultrasonic cleaner, the solution was diluted with distilled water up to 50 ml. After taking an aliquot of 5 ml into a separatory funnel, 5 ml of Zephiramine solution was added to the funnel. An ion-pair complex of I_3^- was extracted into 20 ml of chloroform by shaking for 1 min. The absorbance of the extract was measured at 364 nm. This procedure is called procedure (1). Procedure (2) involved the case in which KI was added to the HCl solution after dissolving the sample in the solution; others were the same as described in procedure (1).

Results and Discussion

Principle of Determination of Copper Valence with KI. The reactions utilized for the determination of Cu^{2+} and Cu^{3+} with KI are as follows:

$$Cu^{2+}+2KI=CuI+1/2\,I_2+2K^+ \tag{1}$$

and

$$Cu^{3+}+3KI=CuI+I_2+3K^+. \tag{2}$$

In the absence of KI,

$$2Cu^{3+}+H_2O=2Cu^{2+}+2H^++1/2\,O_2. \tag{3}$$

When a solid sample was dissolved with an HCl solution containing KI, Cu^{2+} and Cu^{3+} reacted with KI according to Eqs. 1 and 2. The liberated I_2, corresponding to the sum of the valence change of copper, was determined by extraction as a I_3^- ion pair. This corresponded to procedure (1).

On the other hand, Cu^{3+} reacted with H_2O so as to be changed into Cu^{2+} without using KI, according to Eq. 3.

Then, KI was added to the solution containing Cu^{2+}. The Cu^{2+} reacted with KI according to Eq. 1, so as to liberate I_2. Similarly, the amount of I_2 corresponding to the total Cu^{2+} content was determined by extraction. The latter corresponds to the procedure (2). From the values obtained by procedures (1) and (2), the average valence of Cu^{2+} and Cu^{3+} were, respectively, calculated as described latter.

Determination of I_2 by Spectrophotometry. Many kinds of methods for the determination of I_2 or I^- have been reported. Almost all of them are methods designed for the determination of the total iodine content in inorganic or organic materials, water, biomaterials or environmental samples.[8] The determination of a small amount of I_2 in the presence of a large amount of I^- was not investigated in detail, since the titration method of I_2 with a $Na_2S_2O_3$ solution was sufficiently accurate for large amounts of samples. Therefore, the determination method of I_2, in which I_3^- exists in the presence of a large amount of I^-, was examined in terms of spectrophotometry. When spectrophotometry was adapted to a direct determination of I_3^- in the aqueous phase in place of titration, the obtained absorbance was unstable during the measurements of I_3^-, since some organic impurities in the aqueous phase could have reduced the liberated I_2 to I^- ion. Subsequently a part of the large amount of I^- ion could have been oxidized to I_2 by air and/or oxygen in the aqueous phase, as shown in Fig. 1. The unstable results concerning the absorbance resulted in serious faults due to the small amount of samples.

Fortunately, we succeeded in finding the extraction of I_3^- to stabilize the absorbance of the extract (I_3^- complex), owing to separate I_3^- ions from the aqueous phase containing a large amount of the I^- ion (curve 2 in Fig. 1).

Extraction of I_3^- Ion. Iodine (I_2) can be extracted into chloroform at a level of above 90%. However, I_3^- cannot be extracted into organic solvents if the counter cation is not added to the solution containing I_3^- for the purpose of enhancing I_3^- extraction. In this case, the Zephiramine cation ($Zeph^+$) was added to the sample solution containing I_3^-. As a result, I_3^- was extracted into a chloroform solvent as a $Zeph^+I_3^-$ complex. This phenomenon had been reported as an incidental one in connection with the ion pair extraction of metal iodides.[9] However, the extraction conditions for an analysis of Cu^{2+} and Cu^{3+} have not been studied.

In this study, Zephiramine was used as a 0.04% aqueous solution. We added 5 ml of the solution to the sample solution per one extraction. The extracted $Zeph^+I_3^-$ complex showed maximum absorptions at 294 and 364 nm (Fig. 2, curve 2). Curve 1 in Fig. 2 shows the spectrum of the I_3^- ion in the aqueous phase. We selected 364 nm as a measurement wavelength, owing to the reproducibility. Cu(I,II) and their iodides were not extracted into chloroform, and did not interfere with the determination of I_3^-.

Effect of HCl Concentration. At first, a sample must be dissolved with an acid solution. HCl was selected as an acid for dissolving the sample, since HCl does not behave as an oxidant for the I^- ion, and does not function as a precipitant for the Ba^{2+} ion. The effect of the HCl concentration was examined regarding the extraction of I_3^- over the range of 0.1—3 M. We used 5 ml of 0.1—3 M HCl in order to dissolve the sample. The HCl solution containing the sample was then diluted to 50 ml with water. After all, the extraction of the I_3^- ion pair complex was carried out with one tenth the concentration of the HCl solution used for dissolving the sample. Figure 3 shows the effects of the HCl concentration (5 ml) used for dissolving the sample. The absorbance obtained increased with an increase in the HCl concentration used. As a result, 0.1—0.5 M HCl can be recommended because of the low value of the reagent blank.

Bubbling with nitrogen gas was of little use to eliminate oxygen from the HCl solution in the low range of

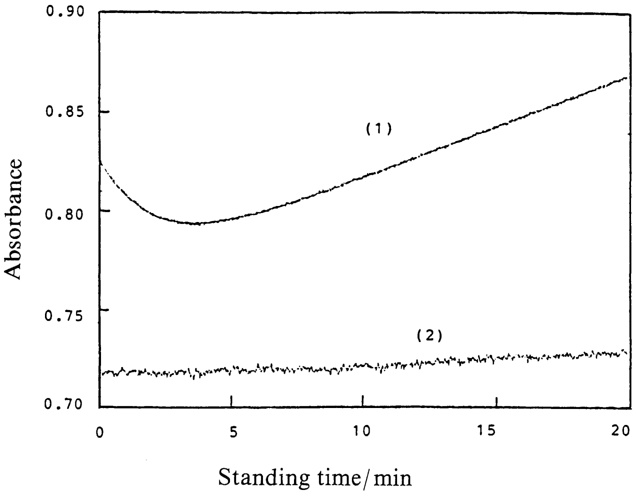

Fig. 1. Effect of the standing time on the absorbance of the I_3^- ion.
(1) I_3^- ion in the aqueous phase, KI: 1 g, Cu^{2+}: 225 μg/50 ml, wavelength: 351 nm,
(2) $Zeph^+I_3^-$ ion pair extracted into chloroform, KI: 1 g, Cu^{2+}: 67 μg, chloroform: 20 ml, Zephiramine: 0.04% 5 ml, wavelength 364 nm,
Reference: H_2O.

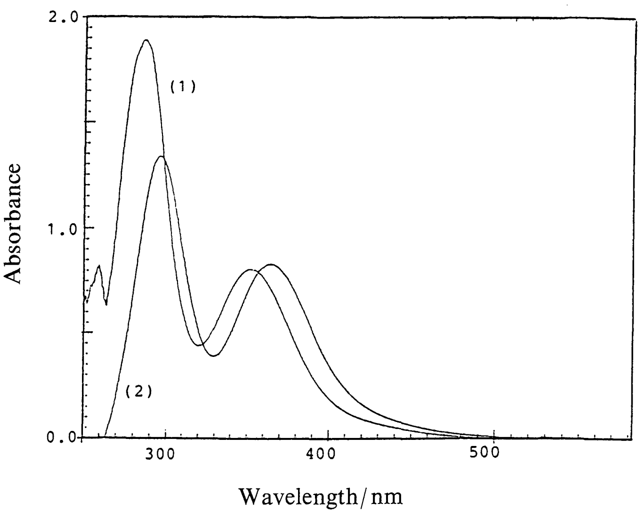

Fig. 2. Absorption spectra.
(1) I_3^- ion in the aqueous phase, Cu^{2+}: 220 μg/50 ml,
(2) $Zeph^+I_3^-$ ion pair extracted into chloroform, Cu^{2+}: 75 μg,
The other conditions are identical to those described in Fig. 1.

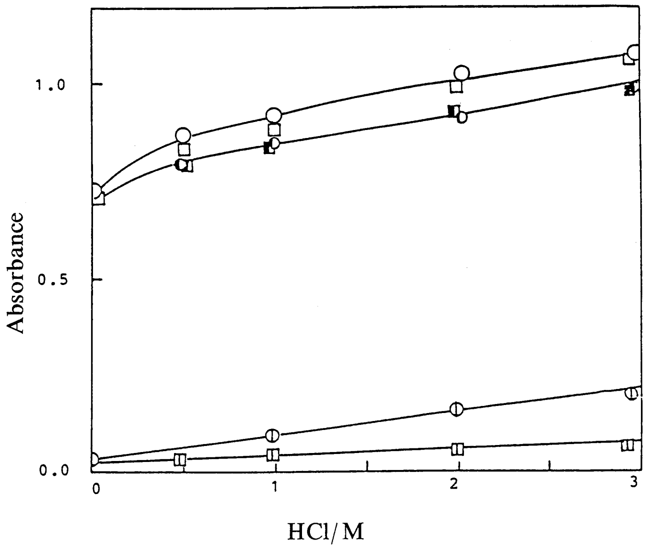

Fig. 3. Effect of the HCl concentration used for dissolving the samples.
Procedure 1: —□— —◧—
Procedure 2: —○— —◐— —⦶— —◫—
Bubbling time with N_2 gas:
20 min; —◐— —◧— —◫—
0 min; —○— —□— —⦶—
Cu^{2+} 764 μg (used as $CuSO_4 \cdot 5H_2O$);
—○— —◐— —□— —◧—
Cu^{2+} 0 μg; —⦶— —◫—
KI: 1 g, HCl solution: 5 ml, Reference: H_2O.

the HCl concentration examined, as is shown in Fig. 3.

Effect of Volume of HCl Solution Used for Dissolving the Sample. The HCl concentration used for dissolving the sample had been kept at 0.5 M. The effect of the volume of the HCl solution was examined over the range from 5 to 40 ml. The absorbance of I_3^- due to the presence of oxygen in the aqueous phase increased with an increase in the volume, as is shown in Fig. 4. However, bubbling by N_2 gas was not carried out in order to eliminate the oxygen from the HCl solution. This was due to the fact that the effect of oxygen in the aqueous phase could be neglected by using 5 ml of the diluted HCl solution.

Copper sulfate pentahydrate was used as a standard sample; nevertheless, the difference between the procedures (1) and (2) increased with an increase in the volume of the HCl solution. These results shown in Fig. 4 could be explained by the roles of copper and hydrogen ions, as follows:[10]

$$Cu^{2+} + O_2 = CuO_2^{2+} \tag{4}$$

and

$$CuO_2^{2+} + 4H^+ + 6\,I^- = CuI + 5/2\,I_2 + 2H_2O. \tag{5}$$

It is recommended to use an amount and concentration of HCl solution that is as small as possible. In the present paper, 5 ml of 0.1 or 0.5 M HCl was used, according to the results described above.

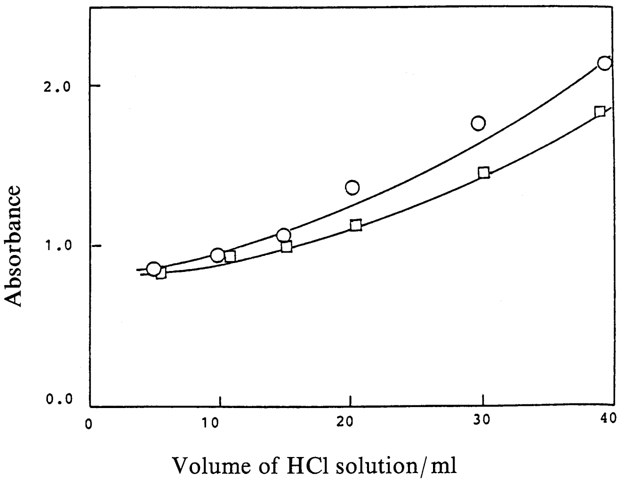

Fig. 4. Effect of the volume of the HCl solution used for dissolving the samples.
Procedure: 1 —□—, 2 —○—
HCl solution: 0.5 M, $CuSO_4 \cdot 5H_2O$: 3.00 mg
KI: 1 g, Reference: H_2O.

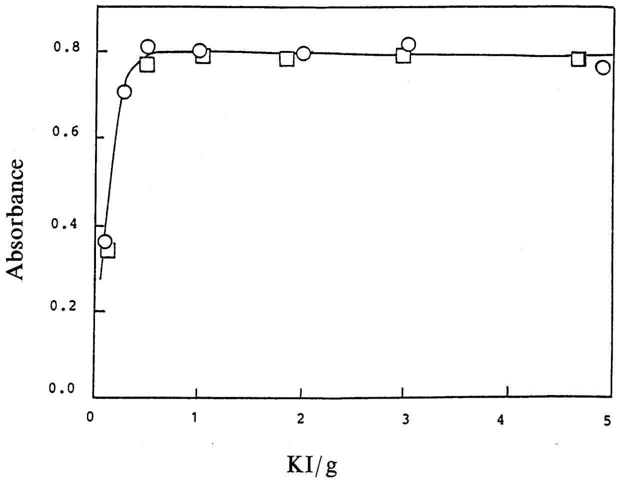

Fig. 5. Effect of the amount of KI.
Procedure: 1 —□—, 2 —○—
Bubbling time with N_2 gas: 20 min, $CuSO_4 \cdot 5H_2O$: 3.00 mg, 0.5 M HCl: 5 ml, Reference: H_2O.

Effect of Supersonic Irradiation. The effects of supersonic irradiation were found after 5 min. Especially, when an HCl solution of dilute concentration (for example, 0.1 M) was used, the effects were significant for an enhancement of sample dissolving.

Effect of Amount of KI. The amount of KI was required to be above 0.5 g in the case of using 5 ml of 0.5 M HCl. The absorbance obtained below 0.5 g of KI showed low values (Fig. 5). In the present study, 1 g of KI was used during the measurements.

Extractability of the $Zeph^+I_3^-$ Ion Pair into Chloroform. The shaking time for the extraction of the $Zeph^+I_3^-$ ion pair was sufficiently above 1 min. Although the extractability of the $Zeph^+I_3^-$ ion pair was

Table 1. Average Valence of Copper in Superconductor Y–Ba–Cu–O

Sample	Present method	Conventional method (Titration)
A	2.26±0.05	2.29±0.03
B	2.25±0.05	2.23±0.04
C	2.23±0.04	2.18±0.04
D	2.25±0.03	2.24±0.03
E	2.17±0.03	2.21±0.01
Samples taken	4—6 mg	60—100 mg

95%, the reproducibility of the result was not very good. This is because the value was calculated by using the conventional method[11] from the result of the second extraction of I_3^-, which remained in the aqueous phase after the first extraction.

Calibration Curve. The calibration curve was constructed under the best conditions (by the Standard Procedures (1) and (2)). The range used for the determination for Cu^{2+} was from 0.05 to 2.5 mg (0.103—2.568 as absorbance). This range corresponds to about 0.2—10 mg of a Y–Ba–Cu–O sample. The coefficient of the correlation over that range was 0.9994. The water was used as a reference for measuring the absorbance. The value of the reagent blank was 0.053 on the absorbance.

Analysis of Y-Ba-Cu-O Sample. The average valence (P) of copper in Y–Ba–Cu–O samples was calculated using the following equation:

$$P=[(A_1/W_1)/(A_2/W_2)]+1.$$

Here, A_1 and A_2 are the absorbances obtained by procedures (1) and (2), respectively. W_1 and W_2 are the weights (ca. 2 mg) of samples used in procedures (1) and (2), respectively. Three measurements of the Y–Ba–Cu–O sample were carried out in order to obtain an average value. The results obtained by the present method are shown in Table 1, and agree with those of the conventional method.[3]

Determination of Cu Ion with Cuproine. The present method effectively utilizes only one tenth of the sample taken. When the remaining sample solution is used to determine the total copper concentration, the sample used by procedure (2) is not required. It has therefore been investigated whether the determination of copper in the sample solution remained in a 50 ml volumetric flask after procedure (1) was carried out.

Cuproine is one of the high-selectivity reagents used for the Cu(I) ion. The conventional procedure by the reagent was available for the determination of copper.[12] The calibration curve was linear up to 100 μg of Cu. The other components comprised metal ions; that is, Y, Ba, and Sr did not interfere with the determination of Cu. The average valence (P) was calculated as follows:

$$P=[(\text{amount of Cu obtained with KI by procedure(1)})/(\text{amount of Cu obtained with Cuproine})]+1.$$

The amount of sample taken decreased to one half that used by the standard procedure described above. The analysis results obtained concerning the samples agreed with those of the standard procedure.

As a result, the amount of sample used for the analysis of copper valence could be decreased down to a total of 4 mg for one measurement by procedures (1) and (2). Further, the amount of sample could be decreased to 2 mg by using the modified method involving cuproine procedure.

This work has been partly supported by a Grant-in-Aid of Scientific Research on Chemistry of New Superconductors.

References

1) H.Takagi, S. Uchida, H. Iwabuchi, H. Eisaku, K. Kishio, K. Kitazawa, K. Fueki, and S. Tanaka, *Physica, B+C (Amsterdam)*, **148B**, 349 (1987).

2) H. Takagi, S. Uchida, H. Iwabuchi, S. Tajima, and S. Tanaka, *Jpn. J. Appl. Phys., Ser. 1,* **1988**, 6.

3) A. I. Nazzal, V. Y. Lee, E. M. Engler, R. D. Jacowitz, Y. Tokura, and J. B. Torrance, *Physica C (Amsterdam)*, **153—155**, 1367 (1988).

4) R. J. Cava, B. Batlogg, R. B. Van Dover, D. W. Murphy, S. Sunshine, T. Sieyrist, J. P. Remeika, E. A. Reitman, S. Zahurak, and G. P. Espinosa, *Phys. Rev. Lett.*, **58**, 1676 (1987).

5) D. C. Parashar, J. Rai, Prabhat K. Gupta, R. C. Sharma, and K. Lal, *Jpn. J. Appl. Phys.*, **27**, L2304 (1988).

6) K. Kurusu, H. Takami, and K. Shintomi, *Analyst,* **114**, 1341 (1989).

7) M. Oku, J. Kimura, M. Omori, and K. Hirokawa, *Fresenius' Z. Anal. Chem.*, **335**, 382 (1989).

8) F. D. Snell, "Photometric and Fluorometric Method of Analysis, Nonmetals," Wiley-Interscience, New York (1981), p. 290.

9) T. Matuo, J. Shida, and T. Sasaki, *Bunseki Kagaku,* **16**, 546 (1967).

10) M. Oku, J. Kimura, M. Hosoya, K. Takada, and K. Hirokawa, *Fresenius' Z. Anal. Chem.*, **332**, 237 (1988).

11) T. Imai, *Bunseki Kagaku,* **22**, 1361 (1973).

12) H. Onishi, "Photometric Determination of Trace of Metals," Part IIA, 4th ed, Wiley-Interscience, New York (1986), p. 528.