Determination of the Average Valence of Thallium in High-T_c Superconductors by Isotachophoresis

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Capillary-tube isotachophoresis was conducted to determine the average valence of thallium in high-temperature Tl-Ba-Ca-Cu-O superconductor samples. A superconductor sample (5—7 mg) was dissolved in 2.5 ml of 0.3 M (M=mol dm^{-3}) HCl. The solution was diluted to 25 ml with distilled water. By injection of a 50 μl sample solution into the analyzer, thallium(I) was determined at 0.05—5 μg with a relative standard deviation of 3.3%. Hydrochloric acid (5.0×10^{-3} M) and LiCl (1.0×10^{-2} M) were selected as leading and terminating electrolytes, respectively. The order of the mobility of the metal ions was $Tl^+ > Ba^{2+} > Ca^{2+} > Cu^{2+}$. Thallium(III) ion was not detected as a zone. The total of thallium was determined after the reduction of Tl^{3+} to Tl^+ with ascorbic acid. The average valence values of thallium in the superconductors were 2.93—2.97. The interference of the Tl^{3+} ion in the determination of the average valence of copper was examined. When the valence of copper was determined with KI by extraction-spectrometry, the Tl^{3+} ion was found to affect the absorbance of the ion-pair complex extracted into chloroform. The effect of this ion was eliminated by a suitable selection of the wavelength.

The electrical properties of a high-T_c superconductor depend on the oxygen content.[1—4] The oxygen content varies over a relatively wide range according to the conditions of the sample preparation, resulting in an oxygen deficiency. It is therefore important to both control and determine the average valence of the metals as accurately as possible when the properties of the high-T_c superconducting oxide are studied. Usually, the oxygen content is calculated based on the valences of the component metals. The determination of the average valences of Cu, Bi, Pb, and Tl, which have variable oxidation states, are especially important for estimating the oxygen content in superconductors. The average valences of a high-T_c superconductor have been determined by iodometry,[5—10] coulometric titration,[11] a Cl_2 generation method,[12] the oxidation of Mn^{2+} to MnO_4^- method[13] and others.[3] However, these chemical methods are not applicable to thallium. The determination of the average valence of thallium has hardly been investigated, other than by XPS[14] and NMR measurements.[15] This is because spectrophotometry using color complex formation cannot accurately distinguish between thallium(I) and thallium(III) complexes. The determination by a redox reaction is difficult, since the redox potential difference between thallium(I) and thallium(III) is not sufficiently large. Therefore, isotachophoresis was conducted in order to determine the average valence of thallium in Tl system superconductors. The thallium ion of the Tl system superconductor was shown to be almost trivalent by XPS.[14] An accurate determination of Tl(I) is thus important for obtaining a reliable average valence.

Experimental

Apparatus and Reagents. Isotachopherograms were recorded with a capillary-tube isotachophoretic analyzer (Shimadzu, model IP-2A) having a potential-gradient detector. The sample weight was determined using a Sartorius micro balance (M3P). The absorbance was measured using a Shimadzu spectrometer (UV-2100S). A thallium(III) solution was prepared with thallium(III) oxide (Wakojunyaku Co., 99.9%). A thallium(I) solution was prepared with thallium(I) nitrate (Kantoukagaku Co., 99%). A copper(II) solution was prepared with copper(II) sulfate pentahydrate (Wakojunyaku Co., Analytical grade). All other metal-ion solutions were prepared with oxides and chlorides (Wakojunyaku Co., Analytical grade). Zephiramine (benzyldimethyltetradecylammonium chloride, Dojindo Laboratories) was used as a 0.1% aqueous solution. All other organic reagents used were of analytical grade.

Procedure. Determination of Thallium(I) and Thallium(III). The sample (5—7 mg) was placed in a 25 ml volumetric flask containing 2.5 ml of 0.3 M (M=mol dm^{-3}) HCl. After the flask had been kept for 10 min in an ultrasonic bath to dissolve the sample completely, the solution was diluted with distilled water to 25 ml (solution A). A 50 μl aliquot was injected using a micro-syringe into the capillary tube of the apparatus; 5.0×10^{-3} M HCl and 1.0×10^{-2} M LiCl were used as the leading and terminating electrolytes, respectively. The lengths of the capillary tube (FEP, i.d. 0.5 mm) and pre-column (PTFE, i.d. 1.0 mm) tube were 10 and 8 cm, respectively. The oven temperature was 15 °C and the migration current was stabilized at 75 μA. The zone lengths of Tl^+ on the chart of the recorder were measured for determining the metal-ion content by calibration. An aliquot of 10 ml from solution A was taken into a 25 ml volumetric flask in order to determine the amount of total thallium ions. Five ml of a 3% ascorbic acid solution was added to the flask. The sample solution was diluted with distilled water to 25 ml. The zone length of the total Tl was determined under the same conditions as for the Tl(I) ion.

Determination of Copper(II) and Copper(III). One gram of potassium iodide was dissolved in 5 ml of 0.1 M HCl in a 50 ml flask. A sample (W1, mg) of Tl-Ba-Ca-Cu-O, 0.4—0.8 mg was put in the flask, which was then placed in an ultrasonic bath for 10 min. The sample solution was diluted with distilled water to 50 ml. An aliquot of 20 ml from the solution was taken into a separatory funnel. Five ml of a Zephiramine solution and 10 ml of chloroform were added to the separatory funnel in order to extract the liberated iodine. After shaking the funnel for 2 min, the absorbance of the separated organic phase was measured at 420 nm. The obtained absorbance was A1.

A second sample (W2, mg) of Tl-Ba-Ca-Cu-O (0.4—0.8 mg) was dissolved in 5 ml of 0.1 M HCl as described above; after the solution was allowed to stand for 10 min, one gram of potassium iodide was added. Then, liberated iodine was determined following extraction with chloroform as described above. The obtained absorbance was A2.

The amount of Cu^{3+} in the sample (W1) was determined based on the difference between A1 and A2(W1/W2). The average valence was calculated using

$$\text{Average valence of copper} = \frac{[\mathrm{Cu}^{3+}]}{[\text{total Cu}]} + 2. \qquad (1)$$

The total Cu should be found so as to determine the average valence of Cu. The total Cu was determined using the solution remaining after an analysis of Cu^{3+}. In this study, the total Cu was determined with bathocuproine by extraction-spectrometry.[13)]

Results and Discussion

Principle for Determining the Average Valence of Thallium. Thallium (I) and (III) ions co-exist stably in an HCl solution. A sample solution was prepared by dissolving the Tl superconductor in an HCl solution. The average valence of thallium in the solution was equal to that of the solid of the Tl system superconductor, since the sample had dissolved without undergoing a redox reaction.[12)] The sample solution was introduced into an isotachophoretic analyzer using a micro-syringe.

An isotachopherogram for a sample solution is shown in Fig. 1. The order of the mobility of the metal ions was $Tl^+ > Ba^{2+} > Ca^{2+} > Cu^{2+}$.

Thallium(III) ion was not detected as a zone because of its very slow mobility. The total thallium was determined after reducing to Tl^+ with ascorbic acid. The average valence of the thallium was calculated using

$$\text{Average valence of Tl} = 3 - 2[\mathrm{Tl}^+]/[\text{Total Tl}]. \qquad (2)$$

The average valence of thallium can also be calculated from Tl^{3+}. However, the results would not be very accurate because of the low concentration of Tl^+ in the Tl system superconductor.

Effects of the Concentration of HCl as the Leading Electrolyte. Hydrogen and potassium ions can be used as the leading ion to determine cations. In this study, the H^+ ion was selected as the leading ion because the mobility of Tl^+ was similar to that of K^+.

The ratios of the gradient (R_E) of Tl^+, Ba^{2+}, Ca^{2+}, and Cu^{2+} were examined by varying the concentration of HCl. The results are shown in Fig. 2. R_E is defined as follows:

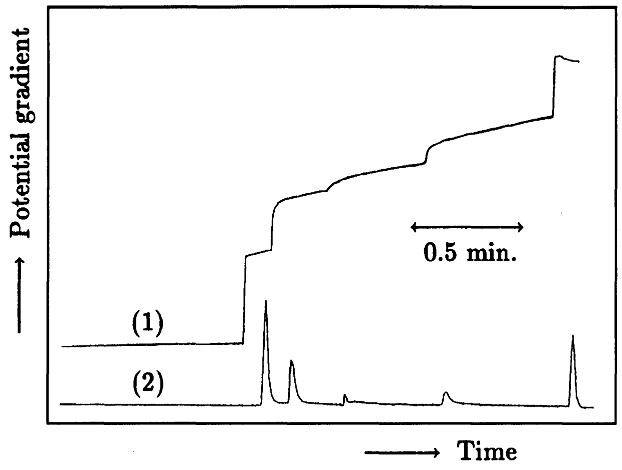

Fig. 1. Isotachopherogram. Tl^+: 0.49 μg/50 μl, Tl^{3+}: 0.99 μg/50 μl, Ba^{2+}: 0.68 μg/50 μl, Ca^{2+}: 0.19 μg/50 μl, Cu^{2+}: 0.19 μg/50 μl. Solvent: 0.03 M HCl, Chart speed: 40 mm min^{-1}, Migration current: 75 μA, Temperature: 15 °C, Leading electrolyte: 5.0×10^{-3} M HCl, Terminating electrolyte: 1.0×10^{-2} M LiCl. (1): Potential gradient, (2): Differential potential gradient.

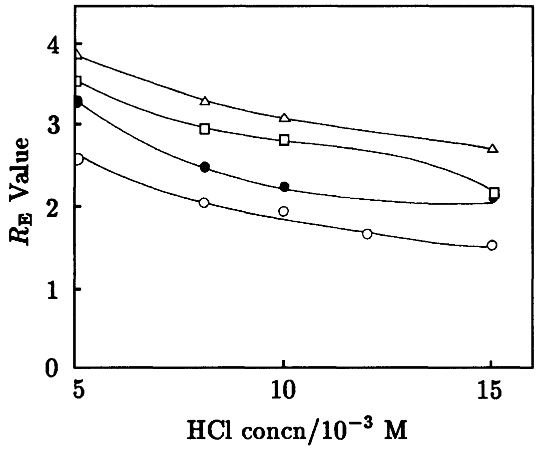

Fig. 2. Effects of the concentration of HCl as leading electrolyte on R_E value. Tl^+: —○— 2.9 μg/50 μl, Ba^{2+}: —●— 1.7 μg/50 μl, Ca^{2+}: —□— 0.6 μg/50 μl, Cu^{2+}: —△— 0.9 μg/50 μl. Solvent: 0.03 M HCl, Chart speed: 40 mm min^{-1}, Terminating electrolyte: 1.0×10^{-2} M LiCl.

$$R_E = h_V/h_L = E_V/E_L = m_L/m_V. \qquad (3)$$

Here, h is the height of the step on the isotachopherogram. E is the potential gradient, m is the effective mobility of each ion, and subscripts V and L denote the ion examined and leading ion, respectively.

R_E of the metal ions decreased with an increases in the concentration of HCl. The interaction among the ions thus increased with the amount of chloride ion. Consequently, R_E should be high at a very low HCl concentration. However, the reproducibility of the zone length was inferior below 4×10^{-3} M HCl. The concentration of HCl was thus made to be 5.0×10^{-3} M.

Effects of the Terminating Electrolyte Concentration. Lithium ion was used as the terminating ion, since the mobility was less than that of the Cu^{2+} ion. A Li^+ solution was prepared with the chloride, and adjusted to pH 5.4. Tris(hydroxymethyl)aminomethane was not used, since it would precipitate Tl^{3+} as hydroxide. The optimal concentration of LiCl was determined from PU on the isotachopherogram at various concentrations of LiCl. PU was obtained as follows:

$$\mathrm{PU} = (h_\mathrm{V} - h_\mathrm{L})/(h_\mathrm{T} - h_\mathrm{L}). \tag{4}$$

Here, subscript T denotes a terminating ion. All other symbols are the same as in Eq. 3.

PU changes with h_T of the terminating electrolyte, as anticipated from Eq. 4. PU varied at a very low concentration of the terminating electrolyte. As shown in Fig. 3, highly constant PU for Tl^+ was obtained at 1×10^{-2}—3×10^{-2} M LiCl. The zone length of Tl^+ was shorter in this range than that below 1×10^{-2} M; thus the sensitivity for Tl^+ determination was low. However, a high PU value gave a low limit of detection. 1.0×10^{-2} M LiCl was thus used as the terminating electrolyte.

Effects of Temperature on the Migration. The zone length for Tl(I) remained constant in spite of a change in the temperature. However, the height of the step in the potential gradient decreased at above 25 °C.

Effects of the Tl^{3+}, Ba^{2+}, Ca^{2+}, and Cu^{2+} Ion Concentrations. When each concentration of Tl^{3+}, Ca^{2+}, and Cu^{2+} was lower than 100 μg/50 μl, the length of the Tl^+ (0.5 μg/50 μl) zone was not affected. However, Ba^{2+} above 5 μg/50 μl decreased the length, as shown in Fig. 4. H^+ ion in the sample solution interfered with any Tl^+ determination above 0.03 M. 2.5 ml of 0.3 M HCl solution were thus used to prepare the sample solution in a 25 ml flask.

The interference of the Ba^{2+} ion was eliminated by using a long capillary tube (the pre-column, 18 cm in length).

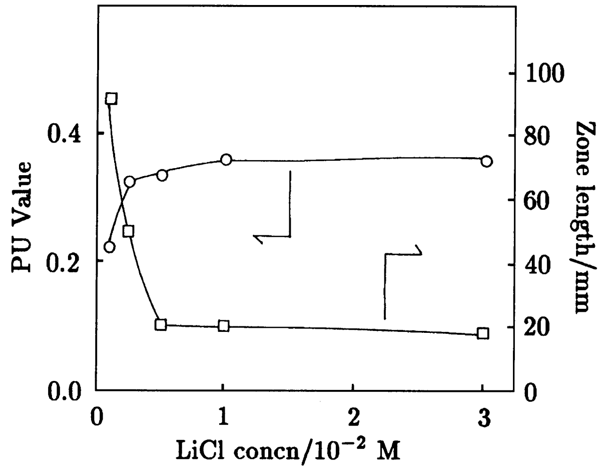

Fig. 3. Effects of the LiCl concentration as terminating electrolyte. Tl^+: 2.01 μg/50 μl, Solvent: 0.03 M HCl, Chart speed: 40 mm min^{-1}, Leading electrolyte: 5.0×10^{-3} M HCl.

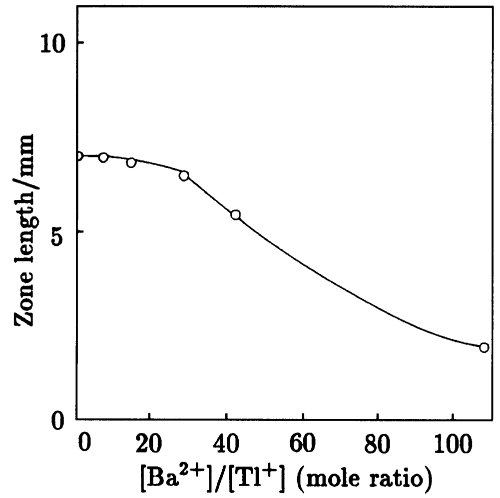

Fig. 4. Effects of Ba^{2+} ion concentration on zone length. Tl^+: 0.494 μg/50 μl, Solvent: 0.03 M HCl, Chart speed: 40 mm min^{-1}, Leading electrolyte: 5.0×10^{-3} M HCl, Terminating electrolyte: 1.0×10^{-2} M LiCl.

Reduction of Tl(III) to Tl(I) with Ascorbic Acid. The thallium(III) ion was not detected under the above-mentioned conditions, since the mobility of Tl^{3+} was less than that of the terminating ion. Tl^{3+} was thus determined after a reduction to Tl^+ with ascorbic acid at 0.2—1.0% as the final concentration (Fig. 5). This concentration did not interfere with the Tl^+ determination.

Calibration Curves for Tl(I) and Tl(III). By the above-mentioned procedures, the thallium(I) and thallium(III) contents were determined at 0.05—5 μg.

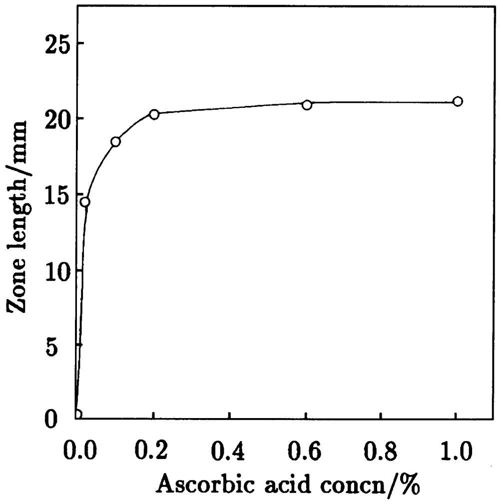

Fig. 5. Effects of ascorbic acid concentration on zone length. Tl^{3+}: 1.99 μg/50 μl, Solvent: 0.03 M HCl, Chart speed: 40 mm min^{-1}, Leading electrolyte: 5.0×10^{-3} M HCl, Terminating electrolyte: 1.0×10^{-2} M LiCl.

Table 1. Average Valences of Tl and Cu in Superconductor Tl-Ba-Ca-Cu-O

Sample	Total Tl/%	Tl^{+} %	Average valence of Tl (n=5)	Total Cu/%	Average valence of Cu (n=5)
A	39.5	0.60	2.97±0.04	12.7	2.25±0.05
B	40.8	0.89	2.96±0.03	12.3	2.20±0.04
C	35.4	0.74	2.96±0.04	9.30	2.13±0.05
D	29.4	1.10	2.93±0.05	14.8	2.15±0.04

Sample taken, Tl: 5—7 mg, Cu: 0.8—1.6 mg.

A linear relationship was observed between the zone length and the thallium concentration within this range. The relative standard deviation for 0.502 μg/50 μl and 0.050 μg/50 μl of thallium was 3.3% (n=9) and 5.0% (n=5), respectively.

A chart speed of 80 mm min^{-1} was selected within a range of 0.05—0.2 μg thallium in order to increase the sensitivity of the determination. The chart speed above 0.2 μg of thallium was usually kept at 40 mm min^{-1}.

Principle for Determining the Average Valence of Copper. In previous studies, this parameter was determined for Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O samples by extraction-spectrophotometry.[7,13] The principle is the same as that for conventional iodometry.

The reactions for the determining Cu^{2+} and Cu^{3+} with KI[12] are

$$\mathrm{Cu}^{2+} + 2\mathrm{I}^- = \mathrm{CuI} + 1/2\mathrm{I}_2 \tag{5}$$

and

$$\mathrm{Cu}^{3+} + 3\mathrm{I}^- = \mathrm{CuI} + \mathrm{I}_2. \tag{6}$$

When a solid sample was dissolved in an HCl solution containing KI, both Cu^{2+} and Cu^{3+} reacted with KI according to Eqs. 5 and 6. Liberated I_2, which corresponds to the sum of the valence change of copper, was determined by extraction as an I_3^- ion pair with Zephiramine ($\mathrm{Zeph}^+\mathrm{Cl}^-$) (procedure I). Cu^{3+} reacted with $\mathrm{H_2O}$ to become Cu^{2+} without KI according to

$$2\mathrm{Cu}^{3+} + \mathrm{H_2O} = 2\mathrm{Cu}^{2+} + 2\mathrm{H}^+ + 1/2\mathrm{O}_2. \tag{7}$$

KI was added to a solution containing Cu^{2+} in order to liberate I_2 according to Eq. 5 (procedure II). The difference in the amount of I_2 in procedures I and II was equal to the amount of Cu^{3+}. The average valence of copper can be calculated from Eq. 1. The amount of the total Cu can also be determined by isotachophoresis. The total copper was determined with bathocuproine by extraction-spectrometry, since this method provided the highest accuracy.

Effects of Thallium(III) on the Valence Determination of Copper. Thallium(III) reacts with KI to be extracted as $\mathrm{Zeph}^+\mathrm{TlI}_4^-$ in chloroform with Zephiramine by the same mechanism as that for I_3^-. The Zeph^+ TlI_4^- ion pair extracted in chloroform affected the spectra of $\mathrm{Zeph}^+\mathrm{I}_3^-$. The additive property between the absorbances of $\mathrm{Zeph}^+\mathrm{TlI}_4^-$ and $\mathrm{Zeph}^+\mathrm{I}_3^-$ did not hold below 410 nm, as shown in Fig. 6. However, the interference of thallium could be eliminated by selecting the wavelength for measuring I_3^-. The additive property held above 420 nm; 420 nm was thus selected as the measurement wavelength in spite of the low sensitivity compared to 364 nm.

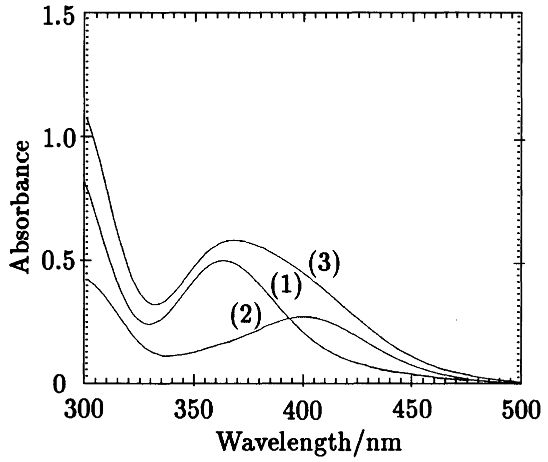

Fig. 6. Absorption spectra. (1) $\mathrm{Zeph}^+\mathrm{I}_3^-$ ion pair extracted into chloroform, Cu^{2+}: 21.0 μg. (2) $\mathrm{Zeph}^+\mathrm{TlI}_4^-$ ion pair extracted into chloroform, Tl^{3+}: 39.4 μg. (3) $\mathrm{Zeph}^+\mathrm{I}_3^- + \mathrm{Zeph}^+\mathrm{TlI}_4^-$ ion pairs extracted into chloroform, Cu^{2+}: 21.0 μg, Tl^{3+}: 39.4 μg. KI: 1 g, Zephiramine: 0.1% 5 ml, chloroform: 10 ml, Reference: $\mathrm{H_2O}$.

Results of Analyses of Tl-Ba-Ca-Cu-O Samples. These results are shown in Table 1. The average valence of thallium in Tl-system samples was 2.93—2.97. The Tl(I) content was less than about 1%. The average valence of copper was 2.13—2.25, a range less than that for a Y-Ba-Cu-O sample.

Tl system superconductor samples were prepared according to the method of Kikuchi et al.[15,16] The sample composition was determined by ICP-AES; the results are given in Table 2. Because of the high vapor pressure of thallium, the thallium content decreased during the sample preparation at high temperature. The superconductor properties were confirmed by T_c and X-ray diffraction.

To determine the average valence of a Tl system superconductor, the sample amount was 5—7 mg. The present method ensures a very accurate determination,

Table 2. Composition of Superconductor Tl-Ba-Ca-Cu-O by ICP-AES (mole ratio)

Sample	Tl/%	Ba/%	Ca/%	Cu/%
A	38.5(1.95)	24.6(1.86)	3.76(0.98)	12.3(2)
B	39.5(2.11)	24.9(1.99)	4.07(1.12)	11.6(2)
C	34.9(1.17)	39.5(1.97)	0 (0)	9.30(1)
D	28.7(1.24)	30.9(2.00)	4.47(0.99)	14.3(2)

$n=3$.

even with small sample amounts.

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