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# Complexing Capacity – A Measure of Evaluating Water Quality

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**Abstract :** Methods for the measurement of copper(II) complexing capacity (CuCC) of natural waters by using the back-extraction of bis(benzoyltrifluoroacetonate)copper(II) and the extraction rate of dithizonato-copper(II) complex were described. Experimental results show that the CuCC of the Kiryu river water samples from urban area were consistently larger than those from up-stream, due to a ligand which originated from human activities.

**Keywords :** Copper(II) complexing capacity, Back-extraction method, Extraction rate method, River water.

## 1. Introduction

Recently, ecological and biological effects of some trace metal ions in natural water have become of major interest. Since the effects of these metal ions depend mainly upon these chemical forms, the speciation of a trace metal becomes more and more important in environmental chemistry [1]. However, in most water systems, the existence of a variety of naturally occurring ligands often makes the equilibrium calculation difficult and the discrimination of a free metal ion from a metal associated with such a ligand is also a task of great difficulty. Under such circumstances, the concept of complexing capacity has been introduced[2-5]. In the case of copper(II) as a trace metal, copper(II) complexing capacity (CuCC) of a water sample is an ability of the sample to remove added copper(II) from the free ion pool[6].

From the above aspects, the authors have developed two different methods for the determination of CuCC. One is the method based on the back-extraction technique using bis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)copper(II). This method enables one to measure the CuCC as well

as the conditional stability constant for the resulting copper(II) complex without any preliminary treatment of a water sample[7]. The second method is based on the extraction kinetics of copper(II) with 3-mercapto-1,5-diphenylformazan (dithizone). In this method, not only the CuCC of natural water samples, but the lability of soluble copper(II) complex can be estimated simultaneously[8]. In this paper, the principle and the application of these methods to river water samples were described.

## 2. Back-Extraction Method

A Schematic diagram of back-extraction method is shown in *Fig. 1*. When the organic solvent which dissolves a copper(II)-chelate ($CuR_2$) is shaken with natural water, copper(II) can be back-extracted into the aqueous phase by forming a complex with a ligand (L) contained in the sample water. The above scheme is feasible only when the newly formed complex in the aqueous solution is more stable than the copper(II)-chelate originally exists in the organic phase. In other words, the use of a highly stable chelate is not suitable for the purpose, because the back-extraction process can not be expected. A water soluble chelate which may cause a positive error should also be avoided. From these considerations, bis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato) copper(II) ($Cu(bfa)_2$) was adopted as a metal chelate dissolved in the organic solvent.

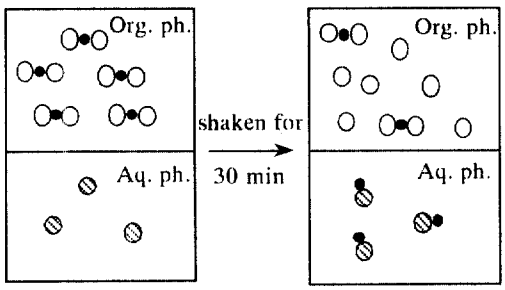


Fig. 1 Schematic diagram of back-extraction method

●: copper(II); ○: chelating agent (R); ⊘: ligand (L)

A recommended procedure for the measurement of CuCC by back-extraction method is as follows; 20 $cm^3$ of the sample was taken in a separatory funnel, and the equal volume of benzene containing $5.00 \times 10^{-5}$ mol $dm^{-3}$ $Cu(bfa)_2$ was added. The mixture was then shaken vigorously for 30 min. After the phases were allowed to separate, the aqueous phase was filtered, and copper(II) in the aqueous phase was determined with an atomic absorption spectrometer. The CuCC value of a water sample is defined as the concentration of copper(II) back-extracted into the aqueous phase.

To ensure the feasibility of the method, the pH dependency of the CuCC was studied by adding a known amount of ethylenediaminetetraacetic acid (edta) into the aqueous phase. As can be seen in *Fig. 2*, the CuCC value is nearly equal to the amount of edta in the pH range of 6.5 to 10. A negligible amount of copper(II) (less than $1 \times 10^{-7}$ mol $dm^{-3}$) was confirmed to be back-extracted into doubly distilled water (blank) in the pH range of 4.8 to 10. Since the pH values of natural waters are in most cases included in the above region, no pH adjustment for the measurement of the CuCC is needed. This feature means that the original equilibrium condition of a water sample is kept unchanged until shaking with the organic phase. Then, the CuCC value obtained by the

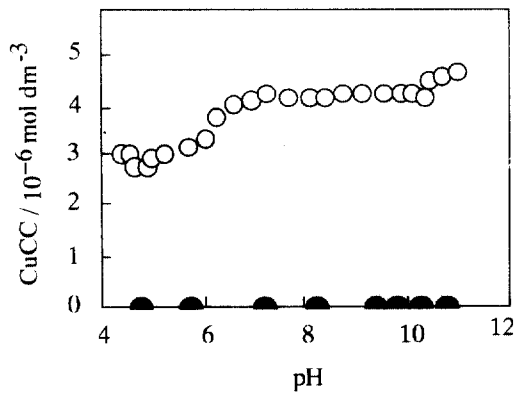


Fig. 2 Effect of pH on the back-extraction method

○ : edta ($5 \times 10^{-6}$ mol $dm^{-3}$) ; ● : blank

present method should indicate the concentration of a ligand whose complexing ability is greater than bfa'.

### 3. Extraction Rate Method

In the case in which a ligand (L) in a water sample forms a complex CuL by adding an excess amount of copper(II) to the water sample, the extraction reaction of CuL with dithizone ($H_2dz$) can be expressed by

$$CuL + 2H_2dz_{org} \rightarrow Cu(Hdz)_{2,org} + 2H^+ + L \quad (1)$$

where the subscript org denotes the organic phase. Assuming that the extraction rate of copper(II) is the first order with respect to CuL, the reaction rate is defined as

$$\text{rate} = v = -\frac{d[CuL]}{dt} = k_{obsd}[CuL] \quad (2)$$

where $k_{obsd}$ represents the observed rate constant for the extraction. Integration results in

$$-\ln[CuL]_t = -\ln[CuL]_{t=0} + k_{obsd}t \quad (3)$$

where the subscript t represents shaking time $t$. According to Eq. (3), a plot of $-\ln[CuL]_t$ against t should give a straight line having a slope of $k_{obsd}$ and an intercept of $-\ln[CuL]_{t=0}$. Here, $k_{obsd}$ and $[CuL]_{t=0}$ were defined as lability of CuL and CuCC, respectively.

A recommended procedure of extraction rate method is as follows; 10 $cm^3$ of a sample solution containing $2 \times 10^{-5}$ mol $dm^{-3}$ copper(II) and 0.1 mol $dm^{-3}$ sodium perchlorate was taken in a separatory funnel, and an equal volume of chloroform containing $5 \times 10^{-4}$ mol $dm^{-3}$ dithizone was added. The mixture was then shaken vigorously for a definite time. After the phases were allowed to separate, copper(II) in the aqueous phase was determined with an atomic absorption spectrometer. According to Eq. (3), the reciprocal of the natural logarithm of the copper(II) concentration was plotted as a function of shaking time, and the values of $k_{obsd}$ and CuCC were obtained from the slope and the intercept of the resulting straight line. All experiments were carried out at room temperature (*ca.* 293 K).

To confirm the feasibility of the proposed method, chelating agents such as nitrilotriacetic acid (nta), edta and citrate were used instead of naturally occurring ligands. The extractability ($E$) of copper(II) in the absence and the presence of the above ligands is plotted as a function of shaking time. The results are given in *Fig. 3*, where it is seen that the extraction rate of copper(II) in the presence of chelating agents is smaller than that of free copper(II) which is quantitatively extracted to chloroform within 5 sec. Therefore, the concentration of copper(II) in the aqueous phase at shaking time $t$ can be assumed to be equal to $[CuL]_t$. A plot of $-\ln[CuL]_t$ against $t$ in which

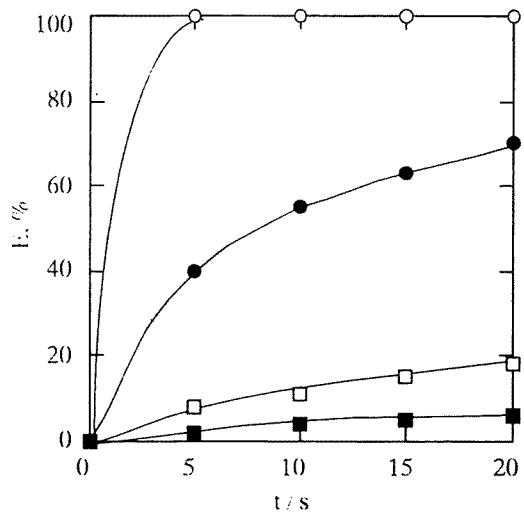


Fig. 3 Plot of extractability (E) of copper(II) against shaking time (t)
○: free copper(II); ●: in the presence of citrate ($2 \times 10^{-5}$ mol $dm^{-3}$); □: in the presence of nta ($2 \times 10^{-5}$ mol $dm^{-3}$); ■: in the presence of edta ($2 \times 10^{-5}$ mol $dm^{-3}$); $[Cu^{II}]$: $2 \times 10^{-5}$ mol $dm^{-3}$; $[H_2dz]_{org}$: $5 \times 10^{-4}$ mol $dm^{-3}$; pH: 7.0

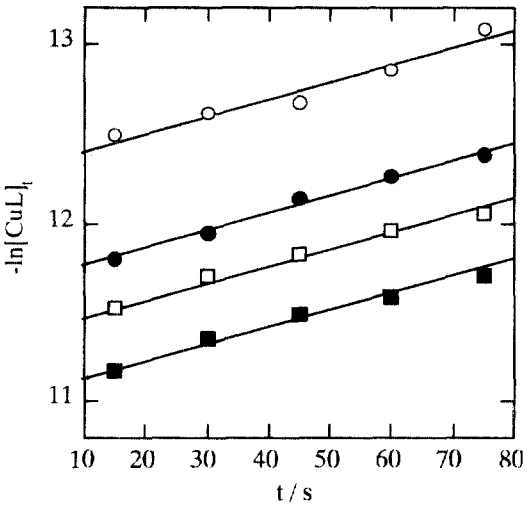


Fig. 4 Plot of $-\ln[CuL]_t$ against shaking time (t) in the presence of nta
Concentration of nta : ○, $4\times10^{-6}$ mol $dm^{-3}$; ●, $8\times10^{-6}$ mol $dm^{-3}$; □, $1.2\times10^{-5}$ mol $dm^{-3}$; ■, $1.6\times10^{-5}$ mol $dm^{-3}$; pH:7.0

nta as a chelating agent is shown in *Fig. 4*, where four straight lines show the validity of Eq. (3). When edta and citrate were used, the plots also fall on straight lines. The $k_{obsd}$ and the CuCC values for the chelating agents obtained by the proposed method are summarized in *Table 1*, where the $k_{obsd}$ values are conditional rate constants under these experimental conditions (pH = 7.0, $[H_2dz]_{org} = 5\times10^{-4}$ mol $dm^{-3}$). The CuCC values approximately agreed with the concentration of ligand added, indicating the usefulness of the method for the estimation of complexing capacity. The $k_{obsd}$ values are independent of the ligand concentration, but depend only on the kind of ligand. This means that one can use the $k_{obsd}$ value for the speciation of naturally occurring ligands.

### 4. Application to River Water Samples

The present methods were applied to river water samples. The water samples were taken from the Kiryu River; the location of point A is up the stream and that of point B is in an urban area (*Fig. 5*). The water samples were filtered using a 0.45 μm membrane filter.

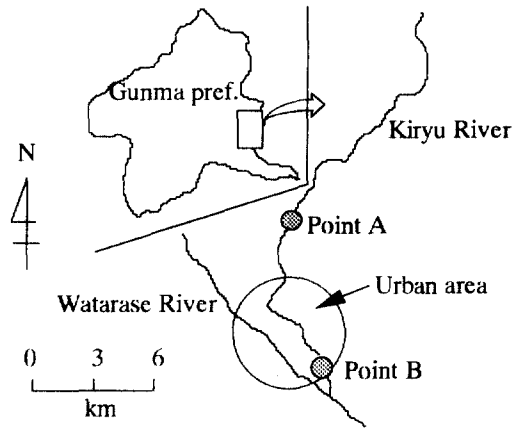


Fig. 5 Sampling locations

Table 1 Copper(II) complexing capacities (CuCC) of water samples containing chelating agents and labilities ($k_{obsd}$) of copper(II)-chelates

| nta | | | edta | | | citrate | | |
|---|---|---|---|---|---|---|---|---|
| $[L]_{added}$ | CuCC | $k_{obsd}$ | $[L]_{added}$ | CuCC | $k_{obsd}$ | $[L]_{added}$ | CuCC | $k_{obsd}$ |
| 4.1 | 4.5 | $9.5\times10^{-3}$ | 4.2 | 4.1 | $8.3\times10^{-6}$ | 5.1 | 3.9 | $8.0\times10^{-2}$ |
| 8.2 | 8.6 | $9.7\times10^{-3}$ | 8.4 | 7.9 | $7.0\times10^{-6}$ | 10.2 | 10.1 | $9.7\times10^{-2}$ |
| 12.3 | 11.1 | $9.5\times10^{-3}$ | 12.6 | 12.0 | $12.2\times10^{-6}$ | 15.3 | 13.1 | $8.1\times10^{-2}$ |
| 16.4 | 15.4 | $9.0\times10^{-3}$ | 16.8 | 16.9 | $8.6\times10^{-6}$ | | | |

$[L]_{added}$, CuCC / $10^{-6}$ mol $dm^{-3}$. $k_{obsd}$ / $s^{-1}$.

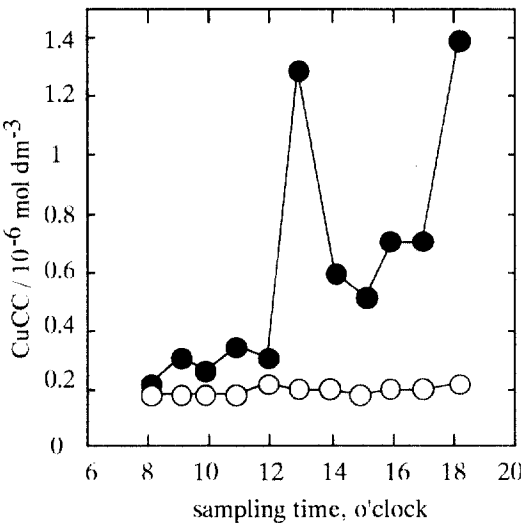


Fig. 6 Hourly change of copper(II) complexing capacity (CuCC) in the Kiryu River water samples
○: Point A; ●: Point B

The results obtained from back-extraction method are shown in *Fig. 6* [9]. Little hourly variation of the CuCC values is seen at point A, whereas the CuCC values obtained at point B are generally higher than those at point A, maxima appearing at 13 and 18 o'clock. The difference in the CuCC values is probably caused by the human activity of Kiryu city located between points A and B. The concentration of naturally occurring ligands is almost constant throughout a day, as is seen at point A. On the other hand, the amount of a ligand originated from the human activity may vary within a day which controls the hourly variation in the CuCC value at point B.

The results obtained from extraction rate method are shown in *Fig. 7* [8]. A plot of -ln[CuL]$_t$ against $t$ consists of two different slopes at point A, indicating

Table II Copper(II) complexing capacity (CuCC) and labilities ($k_{obsd}$) of copper(II) complexes of the Kiryu River water samples

| Point A | | Point B | |
|---|---|---|---|
| CuCC | $k_{obsd}$ | CuCC | $k_{obsd}$ |
| 3.5 | $3.1\times10^{-2}$ | 3.8 | $2.5\times10^{-2}$ |
| 2.1 | $2.5\times10^{-3}$ | 1.2 | $7.9\times10^{-4}$ |
| | | 2.5 | $2.5\times10^{-5}$ |
| Total CuCC | | Total CuCC | |
| 5.6 | | 7.5 | |

CuCC / $10^{-7}$ mol dm$^{-3}$, $k_{obsd}$ / s$^{-1}$

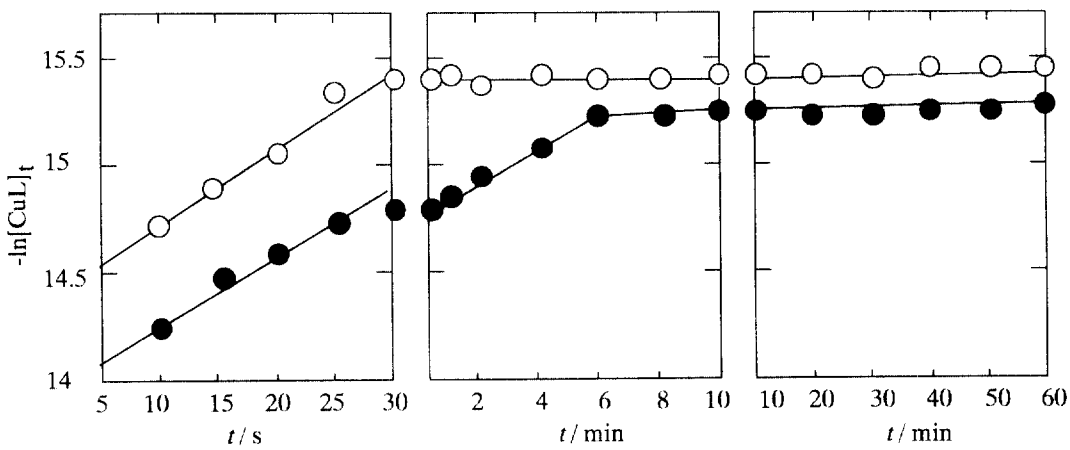


Fig. 7 Plot of -ln[CuL]$_t$ against shaking time (t) in the Kiryu River water samples
○: Point A; ●: Point B; pH: Point A = 6.98, Poin B = 7.01

that two kinds of ligands exist. On the other hand, the plot consists of three different slopes at point B, showing the existence of an additional ligand. The $k_{obsd}$ and the CuCC values obtained are summarized in *Table II*. The total CuCC value obtained from point B is larger than that at point A; such a tendency is consistent with the results obtained from back-extraction method. From the comparison of $k_{obsd}$ values at points A and B, it is estimated that two corresponding ligands are present in water samples from both sampling points. A ligand having intermediate $k_{obsd}$ at point B is absent in the water sample at point A. From this result, we can estimate that a ligand which originated from human activities is present in the point B water. Consequently, larger CuCC values of point B water may be due to the ligand of human activity origin.

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