CHEMISTRY LETTERS, pp. 605-608, 1986.

A NEW METHOD FOR THE MEASUREMENT OF COPPER(II)-COMPLEXING CAPACITY OF NATURAL WATERS BY BACK-EXTRACTION TECHNIQUE

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Back-extraction technique using bis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)copper(II) was introduced to develop a method for the measurement of the copper(II)-complexing capacity(CuCC) and the method was applied to river water samples. Some ligands derived from human activity were found to cause an enhancement in the CuCC-value.

Trace metals exist in various chemical forms in natural waters, and their states may affect the bioavailability. Therefore, the identification of these forms becomes more and more important from the environmental point of view. On the other hand, in most natural systems, a variety of naturally occurring ligands decreases the utility of equilibrium calculations and the determination of a free trace metal ion and a metal associated with such ligands is a task of great difficulty. The concept "Complexing Capacity" has been introduced on the basis of the above situation.[1-4] In the case of copper(II) as a trace metal, copper(II)-complexing capacity(CuCC) of a water sample is an ability of a sample to remove added copper(II) from the free ion pool.[5] Various methods for the measurement of the CuCC have been proposed and reviewed by Hart.[6] However, the chelate extraction has not been applied so far to this purpose. In the present work, a trial was made to establish a new method for determining the CuCC using a chelate extraction system.

When an organic solvent which dissolves a copper(II)-chelate is shaken with a natural water sample, copper(II) can be back-extracted into the aqueous solution by forming a complex with a ligand 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 chelate dissolved in the organic solvent. The established method enables one to measure the CuCC-value as well as the conditional stability constant for the resulting copper(II) complex without any preliminary treatment of a water sample.

A water sample is filtered using a 0.45 μm membrane filter. Twenty cubic centimeters of the resulting sample is taken in a separatory funnel, and the equal volume of benzene containing 5.00×10^{-5} mol dm^{-3} Cu(bfa)$_2$ is added. The mixture is then shaken vigorously for 30 min. After the phases are allowed to separate, the aqueous phase is filtered, and copper(II) in the aqueous phase is determined with a Hitachi 170-30 type atomic absorption spectrometer. The CuCC-value of a water sample is defined as the concentration of copper(II) back-extracted into the aqueous phase.

A negligible amount of copper(II) (less than 0.1 μmol dm^{-3}) was confirmed to be back-extracted into doubly distilled water in the pH range of 4.8 to 10 (Fig. 1). 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 present method should indicate the concentration of a ligand whose complexing ability is greater than bfa$^-$. To ensure the feasibility of the method, the pH dependency of the CuCC was studied by adding a known quantity of EDTA into the aqueous phase. As can be seen in Fig. 1, the CuCC-value is nearly equal to the amount of EDTA in the region of pH above 10. The poor reproducibility is probably due to hydrolysis of copper(II). The CuCC-value seems to decrease along with decreasing pH. This result can be explained by the fact that the complexing ability of EDTA is weakened in the low pH region due to the protonation. The decreasing tendency in the CuCC-value correlates with $\alpha_{L(H)}$, which is the side-reaction coefficient of the protonation toward EDTA anion. In addition, the plot of the CuCC-value against EDTA concentration between pH 7.0 and 9.0 was linear passing through the origin. In conclusion, the CuCC-value obtained by the present method may indicate the complexing ability as well as the concentration of a ligand. The possible existence of HCO$_3^-$ and CO$_3^{2-}$ in natural waters did not affect the CuCC-values in the pH region between 7.0 and 9.0, if the total concentration of HCO$_3^-$ and CO$_3^{2-}$is below 1.0×10^{-3} mol dm^{-3}. However, high contents of HCO and CO$_3^{2-}$ tend to give high CuCC-values, due to the formation of CuHCO$_3^-$ and/or ion pair, Cu^{2+}CO$_3^{2-}$. Among many coexisting cations, iron(III) which is the only possible interfering ion, did not interfere with the determination of the CuCC in the case of its concentration less than 1×10^{-5} mol dm^{-3}.

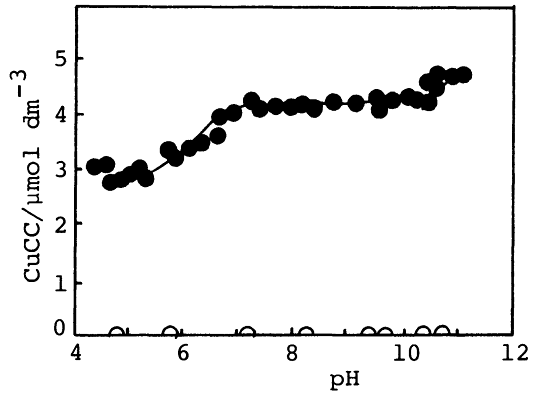

Fig. 1. Effect of pH on the back-extraction of copper(II).

● ; EDTA 5.0 μmol dm^{-3}
○ ; Blank

The present method is applied to the Kiryu river. Water samples were taken at two points (point A is situated 5 km above point B and Kiryu city is in-between A and B) on 7th of November, 1984, and the results are shown in Fig. 2. Little hourly variation of the CuCC-values is seen at point A, except the value of 12 o'clock, just when waste water containing dye from a factory was observed to flow into the river.

The CuCC-values obtained at point B are generally higher than those at point A, maxima appearing at 16 and 22 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 amounts of some ligands originated from the human activity may vary withih a day which control the hourly variation in the CuCC-value at point B. This interpretation will be strengthened by estimating the conditional stability constant for the resulting copper (II) complex in a water sample.

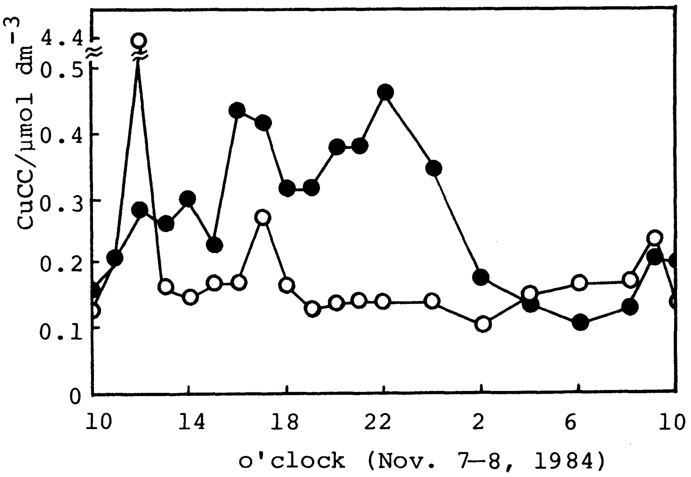

Fig. 2. Variation of CuCC of the Kiryu River within 24 hours.

○ ; point A, ● ; point B

Back-extraction of copper(II) can be expressed by Eq. 1, where the subscript org denotes the organic phase. And the complexation of copper(II) with a ligand, L in a water sample is assumed to proceed according to Eq. 2.

$$\mathrm{Cu(bfa)_{2,org}} \rightleftharpoons \mathrm{Cu^{2+}} + 2\mathrm{bfa^-} \qquad (1)$$

$$\mathrm{Cu^{2+}} + \mathrm{L} \rightleftharpoons \mathrm{CuL} \qquad (2)$$

Equilibrium constants for Eqs. 1 and 2 are defined by K and β, respectively. From the definition of the complexing capacity, CuCC = $[\mathrm{Cu^{2+}}]$+ [CuL]. Since $\mathrm{Cu^{2+}}$ was not detectable in the absence of L , one can assume CuCC = [CuL]. By considering mass balances ($2[\mathrm{CuL}] = [\mathrm{bfa^-}] + [\mathrm{Hbfa}] + [\mathrm{Hbfa}]_{\mathrm{org}}$, $[\mathrm{L}]_{\mathrm{tot}} = [\mathrm{L}] + [\mathrm{CuL}]$) and equilibrium constants (K, β, $K_a = [\mathrm{H^+}][\mathrm{bfa^-}][\mathrm{Hbfa}]^{-1}$, $K_d = [\mathrm{Hbfa}]_{\mathrm{org}}[\mathrm{Hbfa}]^{-1}$), Eq. 3 is obtained, where $\alpha_{\mathrm{bfa(H)}} = 1 + [\mathrm{H^+}]K_a^{-1} + [\mathrm{H^+}]K_dK_a^{-1}$.

$$\log[\mathrm{CuL}] = \log[\mathrm{L}]_{\mathrm{tot}} - \log\left(1 + \frac{4[\mathrm{CuL}]^2}{\alpha_{\mathrm{bfa(H)}}^2 K\beta [\mathrm{Cu(bfa)_2}]_{\mathrm{org}}} \right) \qquad (3)$$

According to Eq. 3, a plot of log[CuL] against $\log[\mathrm{CuL}]^2[\mathrm{Cu(bfa)_2}]_{\mathrm{org}}^{-1}$ should give a curve, which is expected to fit a normalized curve of $Y = -\log(1 + X)$. Thus, the curve-fitting method is applicable to the estimation of β-value. By using the above method, the β-values for soap, dye, and some unknown ligands contained in natural waters were estimated and summarized in Table 1. Since alkylbenzene sulfonic acid does not have any complexing ability, the β-value for a commercial synthetic detergent given in Table 1 suggests that the detergent may contain a certain ligand as an additive. The β-value obtained from a water sample is nearly equal to that for a synthetic detergent. An exceptionally high CuCC-value for a water sample taken from point A may be due to the dye waste, judging from the β-value for a copper(II)-dye complex. In conclusion, some ligands derived from human activity may cause an enhancement in the CuCC-value of river waters. Since a ligand whose structure is unfavorable for forming 1:1 chelate does not satisfy the condition assumed by Eq. 2, an accurate β-value for a fresh water sample that contains only naturally occurring ligand such as fulvic acid can not be estimated by using Eq. 3. It should be noted, however, even for such fresh water samples, the CuCC-values can be obtained by the present method.

Table 1. Conditional stability constants for ligands contained in various samples

Sample	log β
Kiryu River	
point A	4.80
point A[a)]	7.07
point B	5.15
Soap	
No. 1	7.70
No. 2	9.15
Synthetic detergent	
No. 1	3.68
No. 2	4.68
Dye	8.45

a) Sample containing dye.

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(Received January 30, 1986)