Flow-Injection Determination of Complexing Capacity Corresponding to EDTA and Diphosphate Type Ligands for Some Metal Ions

Norio TESHIMA, Hajime YASODA, Makoto KURIHARA and Takuji KAWASHIMA[†]

Laboratory of Analytical Chemistry, Department of Chemistry, University of Tsukuba,
Tsukuba 305-8571, Japan

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Studies of metal speciation are still of great importance in various fields. The reason for this situation is that chemical-speciation data can be used to predict the behavior of trace metals in natural water and to investigate biogeochemical processes.¹⁻³ The measurement of the metal complexing capacity (CC), which is introduced for environmental assessment⁴⁻⁶, is one form of chemical speciation. Reviews on the analytical methods used to measure CC have already appeared.⁷⁻⁹ According to these reviews, previous studies of metal CC in natural water have focused on the measurement of copper CC (CuCC).

During the last decade, numerous methods have also been proposed for measuring the CuCC of naturally occurring ligands using voltammetry¹⁰⁻¹⁴, a back-extraction technique¹⁵⁻¹⁷, ion-exchange¹⁸ and a dialysis membrane.¹⁹ Although the speciation data obtained by these methods are useful to evaluate the toxicity and/or bioavailability of copper, little information from the data can be obtained for other metal ions that are biologically and geochemically important.²⁰

Midorikawa *et al.*²⁰ reported a newly developed method to measure the complexing ability of organic ligands in seawater for copper(II) and cadmium(II): natural ligands in seawater are concentrated and desalted by lyophilization and dialysis, the concentrated solution is electrodialyzed with ethylenediaminetetraacetic acid to remove metal ions using a dialysis membrane, and the demetalized ligands obtained are titrated with copper(II) and cadmium(II) solutions to determine the complexing ability using the corresponding ion-selective electrodes. Chromium(III) binding abilities of humic acid were evaluated by using a cation-exchanger, sulfopropyl Sephadex C-25, in which the cationic unbound chromium(III) species are retained on the resin.²¹ Bidoglio *et al.*²² reported on the complexation of europium(III) and terbium(III) with fulvic acids as well as the competition between aluminum(III) and

europium(III) in a fulvic acid system using time-resolved laser-induced fluorescence. Hawke *et al.*²³ reported an FIA method for the estimation of AlCC of fulvic acids in soil and natural water with photometric detection using Chrome Azurol S: the analytical signal from this method arises from both free aluminum(III) and aluminum(III) bound in labile complexes, but not aluminum(III) bound in non-labile complexes with natural ligands. As described above, few reports concerning various metal CC values obtained by the same method have appeared. Such reports would provide speciation data of individual metals and much information about water analysis.

Recently, we have proposed a reverse FIA (r-FIA) photometric method for the determination of trace amounts of complexing agents such as EDTA, NTA, citrate and diphosphate.²⁴ It is based on the accelerating effect of such complexing agents on the rate of the redox reaction of copper(II) with iron(II) in the presence of neocuproine. In this redox system, a copper(I)-neocuproine complex with an absorption maximum at 454 nm is produced. In addition, we showed that the accelerating effect of these complexing agents on the formation of copper(I)-neocuproine is retarded by adding metal ions such as Al(III), Cu(II), Zn(II), Cd(II) and Pb(II): a decrease in the absorbance at 454 nm is observed. By this phenomenon, a measurement of some metal ion CC of EDTA and/or diphosphate.²⁴ In the present work, several conditions of the method for the measurement of Al(III), Zn(II), Cd(II), In(III) and Pb(II) CC are presented in more detail; especially the InCC is of interest because it is equally obtained for both EDTA-(aminopolycarboxylic acid) and diphosphate-type ligands. The proposed method was evaluated by measuring the CC values of a mixed solution of EDTA and diphosphate.

Experimental

Reagents

All reagents were of analytical-reagent grade and

[†] To whom correspondence should be addressed.

N. T. present address: Department of Applied Chemistry, Aichi Institute of Technology, Toyota 470-0392, Japan.

Fig. 1 Flow diagram of FIA for measuring the complexing capacity. C, acetate buffer solution; S, EDTA and/or diphosphate solution; R₁, iron(II) solution; R₂, a mixed solution of copper(II), neocuproine and acetate buffer; M, metal ion solution (Al(III), Cr(III), Ni(II), Zn(II), Cd(II), In(III) and Pb(II)) involving acetate buffer solution; P₁ and P₂, pump; RC₁, 2.5 cm long coil; RC₂, 100 cm long coil; D, spectrophotometer (454 nm); Rec, recorder; W, waste.

used without further purification. The water used to prepare the solutions was obtained from a Milli-Q water purification system (Millipore, Tokyo, Japan).

Stock solutions of iron(II) (1×10^{-2} M), copper(II) (1×10^{-2} M) and neocuproine (0.1 M) were prepared as described previously.²⁵

Solutions of metal ions injected into FIA system were prepared as follows. Aluminum(III) (0.1 M), zinc(II) (0.1 M) and cadmium(II) solutions were the same as described previously.^{24,26} A chromium(III) solution (0.1 M) was prepared by dissolving 4.00 g of chromium(III) nitrate nonahydrate in 100 ml of water. A lead(II) solution (0.1 M) was prepared by dissolving 3.31 g of lead nitrate in 100 ml of water. Nickel(II) and indium(III) solutions were prepared by diluting stock standard solutions for atomic absorption spectrophotometry with water, respectively. Working solutions of these metal ions were prepared by suitable dilution with a 5×10^{-2} M of acetate buffer solution (pH 5).

Complexing agent solutions of EDTA and diphosphate (0.1 M) were prepared as described previously.²⁶

Apparatus

Figure 1 shows a schematic r-FIA diagram for the measurement of CC. Two double-plunger micro pumps (Sanuki Kogyo, DMX-2000) and a six-way injection valve (Sanuki Kogyo, SVM-6M2) were used to assemble the system. The flow lines were made from PTFE (polytetrafluoroethylene) tubing (1 mm i.d.). The absorbance change was monitored at 454 nm with a spectrophotometer (Soma Kogaku, S-3250) equipped with a 10-mm micro flow cell (8 μ l) and recorded on a recorder (Chino, EB 22005). The pH of the waste solution was continuously monitored with a pH/mV meter (Corning, Model 12).

Procedure

In the flow system as shown in Fig. 1, a 5×10^{-2} M of acetate buffer solution (pH 5) as a carrier solution in

reservoir C, EDTA and/or diphosphate solution in reservoir S, a 1×10^{-4} M of iron(II) solution in reservoir R₁ and a mixed solution of copper(II) (1×10^{-4} M), neocuproine (5×10^{-4} M) and acetate buffer (5×10^{-2} M, pH 5) in reservoir R₂ were pumped at a flow rate of 2.6 ml min⁻¹. An aliquot (375 μ l) of the solution of metal ions (2×10^{-5} M) such as Al(III), Cr(III), Ni(II), Zn(II), Cd(II), In(III) and Pb(II) (M) was injected by the injection valve into the carrier stream (C). A decrease in absorbance at 454 nm was recorded.

Results and Discussion

A redox reaction of iron(II) with copper(II) in the presence of neocuproine proceeds quantitatively, producing a copper(I)-neocuproine complex with an absorption maximum at 454 nm. This redox reaction is extremely accelerated in the presence of complexing agents such as EDTA and/or diphosphate.²⁷ However, the accelerating effect of these two complexing agents on the redox reaction is retarded by adding metal ions such as Al(III), Zn(II), Cd(II), Pb(II) and In(III). In the flow system as shown in Fig. 1, EDTA and diphosphate solutions were pumped as a model ligand in natural water. In the absence of metal ions for the CC measurement, the redox reaction is accelerated in the presence of EDTA or diphosphate. A constant absorbance of the copper(I)-neocuproine complex was obtained. Then, each metal ion was injected into an acetate buffer solution. The metal ion injected reacted with EDTA and/or diphosphate to form a corresponding complex in a reaction coil RC₁, so that a negative FIA peak was obtained. The peak height corresponded to the concentration of each ligand. Thus, the CC values for various metal ions can be determined by measuring the decrease in absorbance at 454 nm.

Various metal ions complexing capacity corresponding to EDTA and diphosphate as model ligands

The CC values of metal ions such as Al(III), Cr(III), Ni(II), Zn(II), Cd(II), In(III) and Pb(II) were measured under the following conditions: $C_{\text{EDTA or diphosphate}} = 1 \times 10^{-5}$ M, $RC_1 = 2.5$ cm, $RC_2 = 65$ cm and $V_{\text{metal ion injected}} = 140$ μ l. In the case of EDTA, the maximum and almost constant values for ZnCC, CdCC, InCC and PbCC were obtained. The AlCC and NiCC values were very low, and the CrCC value was not obtained because the rates of complex formation of Al(III), Ni(II) and Cr(III) were slower than those of other metal ions. In the case of diphosphate, the AlCC and InCC were obtained, while other CC values were not obtainable.

The effects of the EDTA and diphosphate concentrations were examined over the range 2×10^{-6} – 1×10^{-5} M. In the case of EDTA, the InCC, ZnCC, CdCC and PbCC values were the same and linearly increased with increasing EDTA concentration, while the AlCC values were very low. In the case of diphosphate, the AlCC and InCC values linearly increased with increasing

Fig. 2 Effect of the reaction coil length of RC_1 on the CC values. Complexing agents (2×10^{-5} M): ($\circ$), EDTA; ($\bullet$), diphosphate. Other conditions as in the text.

diphosphate concentration, while the ZnCC, CdCC and PbCC values were not obtainable. From the above results, a characterization of complexing agents in natural water samples should be possible by the proposed method; the AlCC values represent diphosphate type ligands, and the ZnCC, CdCC and PbCC values correspond to aminopolycarboxylic acid type ligands. As described later, it is emphasized that the InCC values correspond to two types of ligands.

Effect of the experimental variables

The experimental conditions such as the reaction pH, injection volume of metal ion and lengths of RC_1 and RC_2 were examined by injecting a 2×10^{-5} M solution of each metal ion of Al(III), Zn(II), In(III) and Cd(II). A 1×10^{-5} M of EDTA or diphosphate solution was pumped from reservoir S.

The effect of the pH of the solution on the CC values was examined over the range 4.7–5.6. In the case of EDTA, the maximum and almost constant values were obtained for InCC, ZnCC and CdCC at pH 4.7–5.6. In the case of diphosphate, the AlCC and InCC values rapidly increased with increasing pH of the solution. For the procedure, a pH around 5 was used because the AlCC value with EDTA was relatively low at this pH.

The effect of volume of metal ion solution injected was examined over the range 140–535 μ l. In the case of EDTA, the InCC, ZnCC and CdCC values gradually increased with increasing the injection volume of metal ion solutions, and the AlCC values were very low. In the case of diphosphate, the AlCC and InCC values were obtainable and increased with increasing the injection volume. A 375 μ l of injection volume was selected for the procedure.

Fig. 3 Effect of the reaction coil length of RC_2 on the CC values. Complexing agents (2×10^{-5} M): ($\circ$), EDTA; ($\bullet$), diphosphate. Other conditions as in the text.

The effect of the reaction coil length of RC_1 was examined over the range 1.5–30 cm. The results are shown in Fig. 2. In RC_1 , injected metal ions reacted with complexing agents to form corresponding complexes. In the case of diphosphate, the ZnCC and CdCC values were not obtained, and the AlCC and InCC values gradually increased with increasing the RC_1 length. In the case of EDTA each CC value increased with increasing the RC_1 length, probably because the time of complex formation of each metal ion with EDTA became longer with increasing the RC_1 length. Taking into account the lower value for AlCC, a 2.5 cm long of RC_1 was used for the procedure.

Figure 3 shows the effect of the RC_2 length. The InCC values were almost the same in the cases of both EDTA and diphosphate compared with other metal ions. A 100 cm long of RC_2 was used for the procedure.

Complexing capacity of synthetic mixtures of EDTA and diphosphate

Under the established conditions, the AlCC, InCC, ZnCC and CdCC of synthetic mixtures of EDTA and diphosphate were measured. As shown in Fig. 4, the ZnCC and CdCC values increased with increasing EDTA contents, whereas the AlCC values increased with increasing the diphosphate contents. The InCC values were equally obtained for EDTA and diphosphate type ligand. From these flow signals, EDTA and diphosphate contents were estimated. The results are summarized in Table 1. The contents of EDTA were calculated from the ratio of ZnCC/InCC, and those of diphosphate were calculated from AlCC/InCC. The recovery of diphosphate was found to be satisfactory.

Fig. 4 Flow signals for the CC of mixed solutions of EDTA and diphosphate ($[EDTA] + [diphosphate] = 1 \times 10^{-5}$ M) for Al(III), In(III), Zn(II) and Cd(II). EDTA(%) / diphosphate (%): (a), 50/50; (b), 33/67; (c), 25/75.

The values of EDTA found decreased with decreasing EDTA contents. Although the proposed method was not evaluated in full detail, it is useful for estimating two types of CC in natural water samples.

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Table 1 Estimation of EDTA and diphosphate contents (%) from the CC values

Synthetic mixture ^a		Found	
EDTA	Diphosphate	EDTA	Diphosphate
75	25	91	25
67	33	85	33
50	50	64	49
33	67	44	64
25	75	33	69

a. $[EDTA] + [diphosphate] = 1 \times 10^{-5}$ M.

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