

[OP 1.3]

Radiotracer Techniques for Copper Speciation Kinetics Determinations

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The fate of trace metals in the aquatic environment depends largely on their chemical forms. It has been recognised that not only the equilibrium species distribution (determined by thermodynamic parameters) is of importance, since kinetic parameters of species may influence the behaviour of trace metals as well. In bioavailability and toxicity studies, for instance, information about the *potential* availability of free metal ions is needed rather than a free metal concentration in a state of chemical equilibrium.

Analytical techniques used for the determination of trace metal speciation kinetics include chromatography, voltammetry, and solid-phase extraction. Radiotracer techniques are hardly applied in these types of measurements, although their use may have considerable advantages when combined with the aforementioned techniques. Especially high specific-activity radiotracers of the trace metal under study have proven to be a useful tool. Since a negligible mass of such a radiotracer is added, the preservation of initial chemical equilibria is ensured while easy detection is possible.

High specific activity ^{64}Cu ($t_{1/2}=12.7$ h; γ : 511 keV; $>8\cdot 10^{15}$ Bq g^{-1}) was produced to evaluate speciation kinetics of several Cu complexes. So far, three combinations of radiotracer equilibration and separation techniques have been investigated to determine dissociation rate constants of Cu-EDTA, Cu-NTA, Cu-citrate, Cu-glycine, and Cu-humic acid at pH 6 and an ionic strength of 0.1 mol L^{-1} . Different types of radiotracer equilib-

rium techniques allowed us to follow the speciation kinetics of ^{64}Cu towards or within chemical equilibrium, while ion-exchange or chelating columns provided a way to separate free Cu^{2+} ions from other Cu species. By analysing the experimental results, dissociation rate constants of the complexes could be determined.

The resulting data show that dissociation rate constants of Cu-EDTA, Cu-NTA, and Cu-humic acid are smaller ($<10^{-2}$ s^{-1}) than those of Cu-citrate and Cu-glycine ($>10^{-2}$ s^{-1}). Furthermore, small dissociation rate constants ($<10^{-2}$ s^{-1}) could generally be determined better and more accurate than larger ones. Differences in dissociation rate constants found with different radiotracer equilibration/separation methods will be discussed.

It is clear that the combination of radiotracer techniques with conventional separation techniques is a unique way to study trace metal speciation kinetics. A limiting factor in these experiments was usually the performance of the separation technique itself, rather than the production or availability of the high specific-activity radiotracer.

The expertise obtained with Cu complexes will be used in future work to evaluate the applicability of the technique to other trace metal complexes, viz. Co and Cs complexes. Special attention will be paid to the influence of kinetic parameters on availability of trace metals, e.g. in plant nutrient solutions used in laboratory experiments.

[OP 1.4]

Investigation of the Distribution of Bivalent Metal Ions Among Different Species in Seawater by Sorption on Complexing Resins with Different Sorbing Properties

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A method is proposed for the detection of metal ion complexes in aqueous solution and the evaluation of their reaction coefficients. The concentration of different groups of species can be determined. The method is based on two titrations of the metal ions with two complexing resins with quite different sorbing properties.

Each titration is carried out as previously described [1], based on the relationship: $c = c_{\text{tot}} / (1 + \alpha_M V / K^* w)$, where c is the concentration of metal ion sorbed on the resin, c_{tot} is the total concentration which can be sorbed on the resin, α_M is the reaction coefficient of the metal ion in the solution, in the presence of the resin, and K^* is the ratio of the concentration of metal ion sorbed in the resin phase to the free metal ion in solution after equilibration. It can be evaluated from the sorption equilibria of the metal ion on the resin as previously described [1]. V and w indicate the volume of the solution and resin phase.

Three groups of metal species can be detected, one with a high stability, which is in equilibrium with the strongly sorbing resin, the other with low stability, in equilibrium with the weakly sorbing resin, and a third group of complexes with intermediate stability. The reaction coefficient, or at least its lower and higher limits, can be determined for each group. This information is helpful since it allows comparisons with known systems, providing an idea about the possible nature of the complexes. In the present work, Mn(II), Cd(II), Ni(II) and Cu(II) from different seawater samples were examined simultaneously. The two resins used for the sorption were Chelex 100 and Amberlite CG50. The first is able to strongly sorb the bivalent metal ions, while the other only does so to a much smaller extent. As previously reported [2], the total concentration of the metal ion

is obtained from the titration with Chelex 100. At the same time, the reaction coefficient of the more stable complexes is evaluated. The less strongly sorbing resin, Amberlite CG50, is only able to sorb that metal ion which is combined in relatively weak complexes, or free. In this case, the reaction coefficient can also be evaluated. The concentration of metal ion linked in species with intermediate stability is obtained from the titration curves when a steady value of metal ion is sorbed on Chelex 100 at the highest volumes of the aqueous phase. For these complexes, only limiting values of the reaction coefficients can be evaluated.

The results obtained for two seawater samples, Ligurian Sea and Ross Sea, are presented and compared to give an example of the results obtained. They show large differences in the total concentration and also in the distribution of metal ions between different species. In the case of copper(II), for instance, the concentration in the Ross Sea was much lower than in the Ligurian Sea (164 and 445 ng l^{-1} , respectively), and not any copper(II) was found to be combined in weak complexes with a reaction coefficient lower than $1.0 \cdot 10^2$, since not any copper was sorbed on Amberlite CG50 in the case of the Ross Sea, while this was a large fraction, around 30%, in the Ligurian Sea. In both cases, however, 15% of the copper(II) was combined in species at high stability, with a reaction coefficient of 10^{10} (pH = 7).

[1] PESAVENTO, M.; BIESUZ, R. (1995): Anal. Chem. 67, 3558-3563

[2] PESAVENTO, M., BIESUZ, R., BAFFI, F., GNECCO, C. (1999): Anal. Chim. Acta 401, 265-276