

# On the Chelation of Some Radionuclides in a Sea-water Medium

by

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## 1. Introduction

For the purpose of complete understanding of the chemical cycles of radionuclides in sea water, it is not sufficient to consider inorganic ions or complexes of the radionuclides, but it is also indispensable to take the behaviour of organically bound radionuclides into consideration. There are several evidences which prove that some of the trace metals occur in combination with organic molecules in sea water, although the evidences are somewhat indirect. This aspect of the problem was already reviewed by FUKAI and HUYNH-NGOC [3] in connection with several other aspects of the chemical behaviour of radionuclides in sea water. On the basis of the information obtained up to now it seems important in the future studies to ascertain the origin of organically bound trace elements and to evaluate the quantitative importance of these compounds in the chemical cycles of the trace elements concerned.

In the present study several series of laboratory experiments were carried out in order to examine the possible direct chelate-formation of some radionuclides with organic molecules in sea-water medium. Although a similar attempt was recently made by DUURSMA and SEVENHUYSEN [1] on some trace elements, it seems that it is not always justifiable to draw any decisive conclusion about the chemical behaviour of trace elements in such an extreme dilution as found in sea water on the basis of the results obtained for higher concentrations used in their experiments.

In the experiments presented in this paper more realistic concentrations of metals were used and the time factor of the chelate-formation was especially taken into account. The radionuclides concerned here were manganese-54, cobalt-60 and zinc-65. As a model of chelate-forming organic molecules EDTA. (ethylene-diamine-tetra-acetic acid) was chosen, since the stability constants of the chelate compounds of this substance with many metals were already well established [4] and the substance is popular in use for masking the poisonous effects of traces of some metals in culture solutions of phytoplankton. Therefore, it is clear that the conclusions drawn from the results of these experiments could not immediately be generalized to the chelate-formation *in situ*, yet some suggestions on the general process of the chelate-formation could be obtained.

## 2. Outline of the Experimental Procedures

The solutions for the experiments were prepared in the following manner: the radionuclides concerned (normally 0.2-0.3  $\mu$ Ci) were added to 100-200 ml of distilled water or sea water in the state of divalent ions with 1-50  $\mu$ g of carrier; a small volume of EDTA-solution which contains 0.003 - 1 mg EDTA was added; the pH-value of the solution was adjusted around 8.2; the solution was let to stand for varying periods of time (normally 1-100 hours) under stirring with a magnetic stirrer. After standing about 20 mg of solid manganese dioxide were added to the solution and the stirring was continued for 1 hour. Then the solution was filtered through millipore filter (HA type, pore size 0.45  $\mu$ ). The radioactivity on the filter and in the filtrate was respectively counted by using scintillation well counter. On the basis of these radioactivity measurements the percentage of free ions was computed assuming that only uncombined ions of the metals were adsorbed on the solid manganese dioxide. The percentages thus computed were compared with theoretical values computed by using the stability constants of EDTA-complexes of the metals as the basis.

### 3. Results and Discussions

It has been already known that solid manganese dioxide effectively adsorbs some of radionuclides such as manganese-54, cobalt-60, zinc-65 etc. in sea-water medium [5] and the present author applied this process to the analysis of trace amount of cobalt in sea water [2]. The additional experiments by the present author proved that the metals concerned were not adsorbed on solid manganese dioxide, when they are present in the form of EDTA-complexes. The technique for the separation of chelated fraction of the metals from the uncombined fraction in the experiments stated above may not be strictly correct from the theoretical point of view, since the processes used are rather complicated combination of sorption equilibria, exchange equilibria etc. For the practical purpose, however, the technique could be used without trouble to examine the general trend of chelate-formation of the metals concerned, if the errors of  $\pm 5$  per cent in final results were allowed.

The results obtained in distilled-water medium show that the percentages for uncombined ions of the metals concerned agreed with the theoretical values in the relatively higher range of concentrations (higher than 100  $\mu\text{g}$  element per litre) within several hours of the duration of experiments, while in the relatively lower range of concentrations (lower than 10  $\mu\text{g}$  element per litre) much longer time was required before the equilibrium had been reached. In a sea-water medium the theoretical equilibria could not be reached within 100 hours even in the relatively higher range of concentrations. In these cases, if the equilibria had been reached after 100 hour duration, the activity coefficient of the order between 0.01 and 0.1 would have to be assumed. Of course, for the quantitative theoretical interpretation of these processes the complex-formations of the metallic ions with other ions present in sea water and the equilibria of hydrolysis of the metallic ions have to be taken into account. On the other hand, much more than ten-times of the equivalent quantities of EDTA had to be added in order to cause the chelate-formation within 100-hour duration in the relatively lower range of metal concentrations. These results suggest that the process of the chelate-formation should be a slow process and that the kinetic factor of the reaction would be very important to understand the actual process in a sea-water medium, especially in the lower range of concentrations. If the chelate-formation between these metallic ions and EDTA could be regarded simply as a second order reaction, the period from several months to several years will be required before the equilibrium will have been reached depending on the concentrations of the metals *in situ*. These lengths of time are fairly long for the consideration of the chemical behaviour of radionuclides in the initial period of introduction into sea water, although they are relatively short in comparison with the geochemical cycle of the trace elements in marine environments.

### 4. Conclusions

On the basis of the results and discussions presented above it may be deduced that the possibilities of the direct chelate-formation of the radionuclides concerned with the organic molecules should be small *in situ*, since the uptake of the radionuclides by marine organisms, the sorption by suspended matter, etc. would prevail in the conditions in nature.

### References

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