

Department of Chemistry, University of Antwerp (UIA),
B-2610 Antwerp-Wilrijk, Belgium

Radiochemical Study of Cd, Co and Eu Coprecipitation with Iron Hydroxide in Seawater

R. Chakravorty** and R. Van Grieken*

Abstract. The co-precipitation of Cd, Co and Eu from seawater onto ferric hydroxide was studied, using the radioactive tracers ^{109}Cd , ^{60}Co and $^{152-154}\text{Eu}$, as a function of the pH, the concentration of the collector iron, the concentration of the metal spike and the aging of the internally formed precipitate. For preconcentration purpose, a pH 9 and a 35 ppm iron concentration appeared to be suitable. At pH 8, the natural pH of seawater, the distribution coefficients for Cd, Co and Eu are $10^{4.5}$, 10^5 and 10^7 , respectively.

Key words: coprecipitation, radiotracers, seawater, iron hydroxide, cadmium.

Of the various preconcentration techniques that have been tried for trace element analysis in diverse types of natural and waste-waters, the method of coprecipitation has a widely accepted importance. In the last few decades, various metal oxides and hydroxides have been extensively explored and are still being worked upon for their sorbent properties. One such important sorbent or coprecipitation substrate has been Fe(III) hydroxide which can collect numerous trace elements, itself being speciated in the medium as neutral hydroxide, hydrated ferric oxide [1] or oxyhydroxide [2]. For several trace metal ions, the coprecipitation on iron hydroxide has been studied by the radiotracer technique [3—5] and X-ray fluorescence [7, 8] besides numerous other analytical techniques.

* To whom correspondence should be addressed.

** On leave from: Department of Chemistry, Rammohan College, Calcutta, India.

Also, the predominant role of iron hydroxide, together with manganese hydroxide, as a scavenging agent in the aquatic environment, and in estuaries and seawater in particular, has been documented very clearly in the last decade.

In the present work, we report on a radiochemical study about the coprecipitation of cadmium, cobalt and europium with ferric hydroxide from synthetic seawater under varying conditions. The results allow to optimize the preconcentration procedure for these elements in seawater, namely to find conditions for which the collection yields are high while the enrichment factors are satisfactory, and to assess on a quantitative basis the natural sorption of trace metals on precipitating iron hydroxide. Simultaneously, the coprecipitation behaviour of zinc and manganese was studied using ^{65}Zn and ^{54}Mn tracers. Since the results were identical to those found using X-ray fluorescence analysis as reported earlier [8] and led to same conclusions regarding the optimal preconcentration conditions, they will not be discussed below.

Experimental

Reagents

All the chemicals employed were of analytical reagent grade. Deionised and bidistilled water was used. Stock solutions of FeCl_3 containing 10 mg Fe^{3+}/ml were prepared in 0.5 N HCl. Further dilutions were done by 0.1 N HCl, freshly prepared when needed. The desired concentrations of the metal spikes were obtained as their soluble chlorides, the solution being made in 0.1 N HCl. The radionuclides ^{109}Cd , ^{60}Co and $^{152-154}\text{Eu}$ (in the form of their respective chlorides) of high specific activity were used, appropriate dilutions being made with 0.1 N HCl. Synthetic seawater was prepared according to Kester et al. [9] and preserved at pH 1.8 to 2.0.

Procedure

For measurements at constant volume, the chosen volume of synthetic seawater was 100 ml. First, the desired amount of Fe(III) solution was added, then the amount of metals labelled with the radionuclides. The solution was stirred for 5–10 min to enhance equilibration. The trace ions were next coprecipitated with iron hydroxide at the required pH by adding NH_4OH , and subsequently after settling for 1 h, the precipitate was filtered through a $0.4\ \mu\text{m}$ pore-size Nuclepore membrane. The gamma-activity of the filtrate, about 104 ml, was then counted for 200 s on a $63\ \text{cm}^3$ co-axial Ge(Li) detector, connected to a 4096-channel analyzer. Net counts were obtained by carrying out a correction for dead-time and back-

ground. A standard consisting of an equal amount of radiotracer added to an equal volume (as the final volume of sample filtrate) of the matrix was always counted for the same time under identical conditions to obtain an experimental activity-standard for calculations. The percentage coprecipitation, p , of each metal was calculated as:

$$p = \frac{\text{Activity}_{\text{Standard}} - \text{Activity}_{\text{Sample filtrate}}}{\text{Activity}_{\text{Standard}}} \times 100.$$

The mass distribution ratio D_m was then calculated from:

$$D_m = \frac{\text{amount of element in precipitate}}{\text{amount of element in solution}} = \frac{p}{100 - p}.$$

The distribution coefficient relative to Fe is obtained by multiplying D_m with the ratio of the solution volume (in ml) to the added Fe weight (in g).

Results and Discussion

The co-precipitation was studied as a function of the following parameters: pH, concentration of the collector iron, concentration of the metal spike and aging of the internally formed precipitate. Under the optimized conditions a minimum of 5 replicate experiments were carried out for every parameter checking. For other conditions the number of the replicate experiments was usually 3.

Fig. 1 shows the pH dependence of the coprecipitation yield of Cd, Co and Eu with ferric hydroxide. A pH range from 4.0 to 10.0 was tried. Beyond pH 10.5 no experiment was possible due to clogging of the Nuclepore filter with heavy precipitation of alkaline earths. The metal carrier concentration was 50 $\mu\text{g/l}$ in all cases. The Fe-concentrations were 10, 20 or 35 mg/l. For Eu the coprecipitation is always quantitative with a pH higher than 6. While Cd shows not more than 68% recovery at pH 8.0 and 85% at pH 9.0 even with an Fe-level of 35 mg/l, a 85—95% collection of Co takes place within the pH range 8.0—9.0. Since ferric hydroxide invariably develops a pH-dependent surface charge and the amorphous form, which is typical when precipitated freshly, has its isoelectric point at pH 7.2 in pure water, it is expected to carry down cationic species, dependent on their characteristics, above this value. This isoelectric point depends also on the solution: values between pH 6.0 and 8.5 have been reported [10] and very little is known for solutions of high ionic strength such as seawater. For several ions, the distribution ratios on ferric hydroxides have been reported to

Cd. The decrease of D_m with increasing metal amount is probably the result of the decreasing number of available sites of ferric hydroxide for binding trace ions.

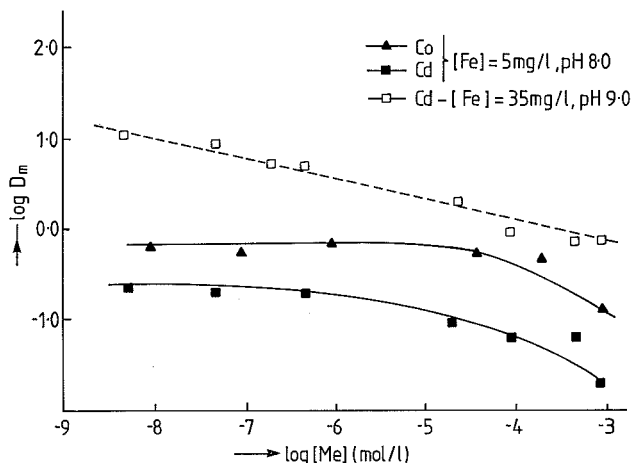


Fig. 3. Influence of initial metal ion concentration on the D_m -value

To study the effect of aging on the recovery yield, iron hydroxide, precipitated together with metal spikes at pH 7, 8 and 9, was left in contact with the solution from 10 min to 30 days. At lower Fe level and for Cd and Co, the $\log D_m$ increases to a maximum level in about 1 h in all cases. No dramatic effect was observed beyond 1 h equilibration time at the pH 9 and 35 mg/l Fe-level. Measurement of the surface area of the precipitate by the BET method did not show any variation between a 1 h and 30 day age either. The possible slow transformation of the amorphous solid phase to thermodynamically more stable forms accompanied by recrystallisation and surface activity changes apparently does not affect drastically the sorption of Co, Cd and Eu by ferric hydroxide. A 1 h equilibration time is thus recommended for preconcentration purposes.

It was also observed that over the pH-range and with individual metal spike concentrations between 0.5 and 50 $\mu\text{g/l}$, the metal ions do not significantly interfere with one another with respect to their percent recovery.

Conclusively, it may be stated that the above discussion supplies useful data for optimised coprecipitation of traces of Cd, Co and Eu over iron hydroxide and on the equilibrium of these elements with iron hydroxide in natural seawater.

Acknowledgement. We gratefully acknowledge the valuable assistance of Mr. L. Van't dack. This work was in part supported by the Belgian Ministry of Health (Management Unit of the Mathematical Model for the North Sea and Scheldt Estuary) in the context of a research project on the environmental effects of iron-acid waste dumping and by the Belgian Ministry of Science Policy (under grant 84-89/69).

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Received October 24, 1986. Revision February 6, 1987.

