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Selective Separation of Cr(VI) from Cr(III) in Seawater by Cobalt-1-pyrrolidinecarboditioate Coprecipitation Method

Kitao Fujiwara,* Shozo Toda,† and Keiichiro Fuwa

Department of Chemistry Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

†*Department of Agricultural Chemistry, Faculty of Agriculture, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113*

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Synopsis. Specific coprecipitation of Cr(VI) in artificial seawater with Co(II)–APDC complex was investigated. The maximum recovery by coprecipitation was 60.6$\pm$4.54% at pH 2 in which Cr(III) was completely separated from Cr(VI).

Historically, determination of Cr(VI)/Cr(III) ratio in seawater is one of the most important subjects, in chemical oceanography. From pure thermodynamic calculation, the amount of Cr(VI) is expected to be over 10^9 times more than that of Cr(III).[1,2] This means almost all chromium will exist in the Cr(VI) state. However, even under oxidative conditions, appreciable amount of Cr(III)[3,4] can be found in seawater. This discrepancy between the thermodynamic calculation and the actual finding of the Cr(VI)/Cr(III) ratio was sometimes explained in terms of the reduction of Cr(VI) by organic substances coexistent in the seawater or due to the catalytic participation of inorganic materials such as manganese nodules. On the other hand, the lack of an analytical method specific to Cr(VI) might also cause this discrepancy.

For Cr(III) ion, hydroxides of iron and zirconium have been successfully applied to seawater analysis.[4,5] Unfortunately, there is no specific method for Cr(VI) ion except solvent extraction.[5–8] However, solvent extraction might not be preferable for Cr(VI) stability because of the possibility that the use of large amount of organic solvent causes the reduction of Cr(VI), and also it is time-consuming when many samples have to be analysed.

In the present note, the coprecipitation with Co–APDC complex, which was first reported by Boyle *et al.*[9] was applied as a selective and specific method for separating Cr(VI) from seawater.

Experimental

As the chromium salts, $K_2Cr_2O_7$ and $Cr(NO_3)_3 \cdot 8H_2O$ were used. When coprecipitation was performed, the artificial seawater of 25—50 ml was taken, and 100 μl of *ammonium 1-pyrrolidinecarbodithioate* (APDC) solution (3%: ≈0.18 M) was added to the sample after adding 200 μl of cobalt solution (0.85 g $CoCl_2$–$6H_2O$/l: ≈0.3 mM). All the experiments in this paper were done with artificial seawater which was prepared according to Ref. 10. Co–APDC suspension was left for about 1 h and centrifuged at 5000 $\text{min}^{-1} \times 20$ min. After drying the centrifuge tube, the precipitate was dissolved in 1 ml of 10% nitric acid solution, and chromium was determined by atomic absorption spectrometry with a carbon rod furnace (a Hitachi 170-50 atomic absorption spectrophotometer with a Jarrell-Ash FLA 100 atomizer).

Results and Discussion

The dependence of coprecipitation recovery of Cr(VI) and Cr(III) on pH of seawater is shown in Fig. 1. The values in the figure were the average of duplicate or triplicate measurements. Cr(VI) is well coprecipitated in the low pH region, being maximum at pH 1—3. When the solution was adjusted to pH 2, the recovery was 60.6$\pm$4.54% (standard deviation for nine independent coprecipitations). This value is almost constant against 0.2—10 ppb of Cr(VI) region. In the present experiment, the samples with Co–APDC suspension were left for 1 h before centrifuging. However, the recovery scarcely changed during the overnight standing of Co–APDC suspension.

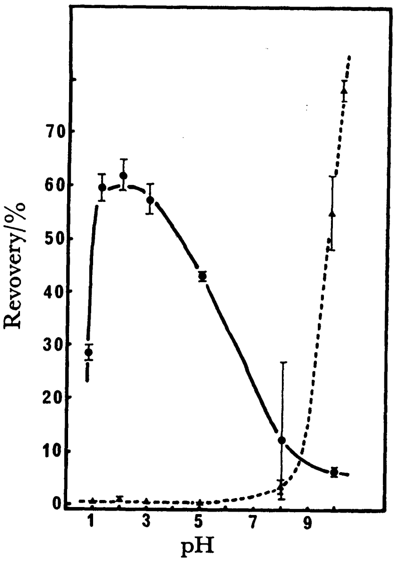

Fig. 1. Dependence of coprecipitation recovery on pH of seawater.

pH of seawater was adjusted by adding hydrochloric acid and sodium hydroxide solution. ●: Cr(VI), ▲: Cr(III).

On the other hand, the amounts of Cr(III) coprecipitated with Co–APDC are negligible at pH regions lower than 5. However, these values increase steeply above pH 9. The Cr(III) coprecipitation at low pH could be considered as contamination due to the incomplete separation of precipitate from the supernatant solution in the centrifugal process.

Figure 2 shows the effect of Cr(III) coexistence on the Cr(VI) coprecipitation. As can be seen in the figure, coexistence of Cr(III) up to 100 times more than Cr(VI) does not disturb the result of coprecipitation of Cr(VI) ion. Since oxidation of Cr(III) to Cr(VI) hardly proceeds in the present condition, the contamination of Cr(III) in the centrifugal separation might cause the increase of signal at the sample which contains 4000 ppm of Cr(III).

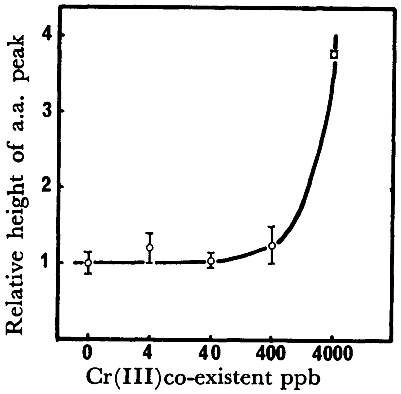

Fig. 2. The effect of Cr(III) coexistence on Cr(VI) coprecipitation.
All the solution contained 4 ppb of Cr(VI), and adjusted at pH 2.

From the present result, it has been confirmed that the cobalt 1-pyrrolidinecarbodithioate coprecipitation technique, which was first proposed for the analyses of Cu, Ni, and Cd in seawater,[9] is also effective for the selective and specific separation of Cr(VI) from seawater. Although the recovery of Co–APDC coprecipitation for Cr(VI) is only about 60%, this value is quantitative and reproducible. Therefore, the present method is a useful technique for the determination of Cr(VI) in seawater.

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References

1) H. Elderfield, *Earth Planet. Sci. Lett.*, **9**, 10 (1970).

2) G. Arrhenius and E. Bonatti, "Progress in Oceanography," (1964), Vol. 3, p. 7.

3) R. Fukai, *Nature*, **213**, 901 (1967).

4) R. Cranston and J. Murray, *Anal. Chim. Acta*, **99**, 275 (1978).

5) A. Satō and N. Saitoh, *Bunseki Kagaku*, **25**, 663 (1976).

6) K. Kazuo, T. Owa, M. Takaoka, T. Tanaka, and A. Kuwahara, *Bunseki Kagaku*, **25**, 122 (1976).

7) S. Osaki, T. Osaki, S. Shibata, and Y. Takashima, *Bunseki Kagaku*, **25**, 358 (1976).

8) T. R. Gilbert and A. M. Clay, *Anal. Chim. Acta*, **67**, 289 (1973).

9) E. A. Boyle and J. M. Edmond, *Anal. Chim. Acta*, **91**, 189 (1977).

10) D. R. Kester, I. W. Duedall, D. N. Connors, and R. M. Pytkowicz, *Limnology and Oceanography*, **12**, 176 (1967).