

The Interaction of ^{51}Cr and EDTA in Sea Water
and NaCl Solutions

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Summary: The behaviour of ^{51}Cr as Cr^{3+} and CrO_4^{2-} in sea water as well as chelation of ^{51}Cr with EDTA in sea water are investigated by high-voltage paper electrophoresis. The results are of importance for chemical speciation and organic chelation of chromium in sea water.

Résumé: Le comportement du ^{51}Cr comme Cr^{3+} et du CrO_4^{2-} dans l'eau de mer et la chelation du ^{51}Cr avec l'EDTA dans l'eau de mer ont été étudiés par l'électrophorèse à haute tension sur papier. Les résultats sont de l'importance pour la formation des espèces chimique et pour la chelation du chromium dans l'eau de mer.

^{51}Cr is one of more abundant radionuclides present in the reactor effluent as a result of a neutron bombardment of the impurities in the introduced coolant or corrosion of metal components of the reactor system. In the case of pollution of ^{51}Cr it is important to define: 1) the particular chemical species of chromium which is involved in the biological accumulation processes, and 2) the interaction of chromium with organic matter.

The interaction of ^{51}Cr with EDTA in sea water and 0.55 M NaCl was investigated by high-voltage paper electrophoresis.

Sea water used originated from the Ligurian Sea (vicinity of Monaco) and from the Adriatic Sea (vicinity of Rovinj), and prior to use was filtered through 0.45 μ membrane filter. In order to compare the behaviour of ^{51}Cr in sea water-EDTA

systems with its behaviour in NaCl-EDTA systems, 0.55 M NaCl solutions were used. The concentration of EDTA was varied from 10^{-6} to 3.3×10^{-2} M. The concentration of chromium added by radioactive ^{51}Cr in the systems was 10^{-6} M, which is far above the concentration level of chromium in sea water (10^{-9} M). In all the systems pH was adjusted to 8.0.

The behaviour of chromium was followed by measuring its electrophoretic mobility of ^{51}Cr in dependence on the EDTA concentration in the systems and on aging of the systems from 0 to 7 days.

Two forms of chromium were introduced to sea water: Cr^{3+} and CrO_4^{2-} . ^{51}Cr in the form of Cr^{3+} gives in sea water mainly nonmobile zone at the starting point of the electrophoretic strip and some tailing in the cationic direction, but not a defined electrophoretic zone. Effect of aging plays an important role; namely, in $t = 0$ day zone at the starting point yields 62% and at $t = 7$ days 98%.

^{51}Cr in the form of CrO_4^{2-} gives in sea water one well defined anionic zone (95%) with electrophoretic mobility $u = 4.25 \times 10^{-4}$ ($\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$), and the second zone at the starting point (5%).

In NaCl solution the behaviour of Cr^{3+} is completely different than in sea water. Besides non-mobile zone Cr^{3+} gives three well defined cationic zones, in 1 day old system even four, but in 7 day old system the most mobile cationic zone (C_1) disappears as a zone, only some tailing remains which does not exceed 1% of the total.

For interaction of ^{51}Cr and EDTA chromium in the form of Cr^{3+} was used. To be sure all chromium was in $3+$ form the radioisotope was boiled with HCl for half an hour. By addition of EDTA to sea water systems anionic tailing appears but even at very high EDTA concentration (3.3×10^{-2} M) all chromium was not chelated with EDTA (only 85% at $t = 1$ day). The aging of the system is significant, e.g. at the EDTA concentration of 10^{-2} M at $t = 0$ day only 6% of chromium is chelated and at $t = 7$ days 28%.

In NaCl-EDTA systems the chelation of chromium with EDTA is more complicated and effect of aging plays also an important role. At the EDTA concentration of 10^{-5} M at $t = 7$ days the fifth cationic zone of chromium (C_5) appears. At the same EDTA concentration also at $t = 7$ days appears a well defined anionic zone A_1 . At

the EDTA concentration of 10^{-3} M at $t=7$ days also appears second anionic zone A_2 . It should be mentioned that in the systems where anionic zones are existing cationic zone C_1 was not found any more.

From the literature it is known that at higher pH values chromium forms two EDTA chelates, $CrY(H_2O)^-$ and $CrYOH^{2-}$, and the pH of this reaction is 7.39 (Ref.1). If we calculated the distribution of those two forms at pH 8, then $CrYOH^{2-}$ should amount to 80% and $CrY(H_2O)^-$ to 20%. Our results show quite a good agreement with those calculated values. If we assume complete chelation, in seven day old system at the EDTA concentration of 10^{-3} M and 10^{-2} M, zone A_1 ($CrYOH^{2-}$) yields 84.67 and 83.67 and 83.13%, respectively. Second zone A_2 should be attributed to the second EDTA chelate, $CrY(H_2O)^-$.

References:

1. G. Schwarzenbach and J. Heller, 1951, *Helv.Chim.Acta* 34, 576.
2. T.M. Florence and G.E. Batley, Trace metal species in sea water I. Removal of trace metals from sea water by a chelating resin, *Talanta* 23 (1976) 179-186.
3. J.J. Morgan, 1967. Application and limitations of chemical thermodynamics in water systems. In "Equilibrium Concepts in Natural Waters", R.F. Gould (Ed.), American Chemical Society Advances in Chemistry Series No. 67, pp. 1-29.

DISCUSSION

Questions and comments:

1. Why do you not ascribe the second anionic zone to the double chelate of Cr with EDTA (Cr : 2 EDTA)?
(B. RASPOR, Yugoslavia)
 - By increasing the EDTA concentration in NaCl solutions at pH 8 we found two anionic zones with different anionic mobilities, A_1 ($u = + 1.07 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$) and A_2 ($u = + 0.74 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$). From the literature data¹ we have calculated the distribution of two anionic Cr-EDTA chelates at pH 8, the form CrYOH^{2-} amounts to 80% and the other one $\text{CrY}(\text{H}_2\text{O})^-$ to 20%. The more negatively charged form corresponds to our A_1 zone, and from experimental data it amounts to 83.9%, the second zone A_2 amounts to 16.1%. In the case of double chelate (Cr : 2 EDTA) the anionic mobility of that zone should be even higher than of the zone A_1 , being more negatively charged (-6). From the other side no evidence in the literature was found about the existence of double EDTA chelate of chromium at those pH values and excess of EDTA.

2. On the basis of the results obtained on Cr interaction with EDTA, can you state any guess what happens in natural sea water? (R. FUKAI, Monaco)
 - Unfortunately, there has been little experimental verification of the presence of dissolved organic complexes of chromium in natural waters. According to the calculations of Florence and Batley² it seems that dissolved Cr(III) reacts quantitatively with EDTA; at the concentration of EDTA of $2 \times 10^{-8} \text{ M}$ 99.8% of Cr(III) is chelated with EDTA (concentration of Cr(III) is 10^{-9} M). According to the theoretical calculations of Morgan³ 0.3% of the total chromium concentration in sea water is present as Cr(III)-EDTA chelate and from all computed organic ligands Cr-EDTA complex is more abundant one.

6. Have you found significant differences between interaction of metal ions with commercial humic material you used before, and marine sediments you studied now? (V. ŽUTIĆ, Yugoslavia)
- We have found some differences in the behaviour of humic acid from marine sediment origin and commercial one, but not significant. It seems that humic acid of marine sediment origin binds the investigated metals at lower concentrations than the commercial one. It should be mentioned that experiments with humic acid of marine sediment origin have been performed in more detail. Moreover, systems with diluted sea water were prepared in order to simulate the estuarine conditions.
7. It seems that the people are rather disappointed with the fact that humic acid are not such strong chelating agent as it was expected. Due to the predominant chelation of dissolved humic material with Ca and Mg cations in sea water there should not be a significant difference in complexing ability between terrestrial and marine sediment humic substances. As the experimental results with NTA showed, a large amount ($- 3 \times 10^{-4} \text{M}$) of NTA is necessary to chelate only 20% of total Cd concentration ($3 \times 10^{-9} \text{M}$) and as it is known, NTA is rather strong chelator having significantly higher stability constant with the trace metals Cd, Pb and Zn than humic acid. (B. RASPOR, Yugoslavia)
8. Have you measured freshly mixed systems; what was the effect of aging? (V. ŽUTIĆ, Yugoslavia)
- Effect of aging seems not to play an important role in the binding of metals with humic acid, although in the case of commercial humic acid in NaCl solutions, in other systems some decomplexing of Pb-humates occurs at the concentration of 20 mg humic acid/l. At higher humic acid concentration no effect of aging was found any more.

