

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

Lj. Musani and Z. Konrad
Center for Marine Research, "Rudjer Bošković" Institute
Zagreb, Croatia, Yugoslavia

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, *Helv. Chim. Acta* 34 (1951) 576.
2. T.M. Florence and G.E. Batley, *Talanta* 23 (1976) 179.
3. J.J. Morgan, 1967. Applications 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.

MUSANI, L., KONRAD, Z.

"The interaction of ^{51}Cr and EDTA in sea water and NaCl solutions"

Paper presented by L. Musani (Yugoslavia)

Discussion

B. RASPOR: Why don't you ascribe the second anionic zone to the double chelate of Cr with EDTA (Cr:2EDTA)?

L. MUSANI: 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:2EDTA) the anionic mobility of that zone should be even higher than that 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.

R. FUKAI: On the basis of the results obtained on Cr interaction with EDTA, can you state, by guess, what happens in natural sea water?

L. MUSANI: 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 among all computed organic ligands Cr-EDTA complex is the most abundant.

