Complexation of ^{212}Pb with Humic Acids

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The complexation of Pb(II) with humic acids (HA) was studied at metal concentrations ranging from 1 * 10^{-9} up to 1 * 10^{-5} mol/l and at a constant humic acid concentration of 10 mg/l. For the first time, the radionuclide ^{212}Pb was used for these studies. The total Pb content of all solutions was controlled by ICP-MS. The natural purified Aldrich-HA and a synthetic HA (M42) were used at pH 5 and 6 [1, 2]. The indirect speciation - separation of the free metal ion and complexed metal ion - was performed with the anion-exchange resin Sephadex DEAE A-25 in batch experiments [3]. The stability constants were calculated by the metal-ion-charge-neutralization-model [4].

The short-lived radionuclide ^{212}Pb ($T_{1/2}$ = 10.64 h) was isolated from the Th decay chain. A ^{228}Th / ^{220}Rn / ^{212}Pb - generator was used as illustrated in figure 1. $^{228}Th^{4+}$ (~500 kBq) was coprecipitated with Zr^{4+} and sodium stearate. The precipitate was filtered, washed and dried as a circular pellet. This was placed at the bottom of a titanium/polyethylene chamber. At the top of the chamber a Pt - foil closed the generator. A high voltage of 450 V was used between the titanium base and the Pt - foil. The ^{228}Th decay product ^{220}Rn escaped in the chamber from the precipitate by emanation. The ^{220}Rn decay product ^{212}Pb was electrodeposited on the Pt - foil for 10 - 20 hours (1 - 2 half lives of ^{212}Pb). The ^{212}Pb was dissolved by rinsing the Pt - foil three times with 100 µl 1 M $HClO_4$ for 10 min at room temperature. These three fractions were combined to the ^{212}Pb stock solution. The ^{212}Pb activity was measured with a Ge-detector at 239 keV. A comparison between the measurements of the foil before and after the dissolution gives a radiochemical yield of about 60 % for the stock solution. The lyophilized HA were dissolved with a few drops of diluted NaOH and these solutions were filled up with buffer to a stock solution of 1 g/l HA. In addition to the ^{212}Pb, known amounts of non-radioactive Pb (1 * 10^{-9} - 1 * 10^{-5} mol/l) were contacted with the HA. All Pb ion / HA solutions were buffered with 10^{-3} M MES at an ionic strength of 0.1 M $NaClO_4$ (pH 5 and 6) and were allowed to stand for 20 hours to reach chemical equilibrium. The total Pb concentrations were determined with ICP-MS (mass 208). The anion-exchange resin Sephadex DEAE A-25 was washed in batch with analytical-analogue solution until the supernatant had the same pH and conductivity as the analyte solution (Pb ion / HA). 200 - 400 mg of the resin were shaken 30 seconds with 4 ml of analyte solution and 2 ml of the supernatant and the activity in the original solution were measured by γ-spectrometry.

The determination of the non-radioactive Pb content of all ^{212}Pb / HA solutions by ICP-MS gave a Pb background of 9 * 10^{-9} mol/l in the solutions without addition of non-radioactive Pb, independend of the HA used. This contamination with non-radioactive Pb is caused by the content in Pb of the chemicals (MES, $NaClO_4$, NaOH and $HClO_4$ for pH adjustment). This Pb concentration was taken into consideration for the complexation experiments. The dependence of the complexation constant log β_{LC} on the total Pb concentration is shown in figure 2. There are no significant differences in the complexation constants between choosen pH or type of HA. We could not observe a significant increase in the complexation constant with decreasing Pb concentrations as it was previously determined for Np(V) [3]. Due to the contamination of the analytical solutions with non-radioactive Pb from the chemicals we could not reach the concentration range of 10^{-15} - 10^{-10} mol/l, as originally aimed in this work.

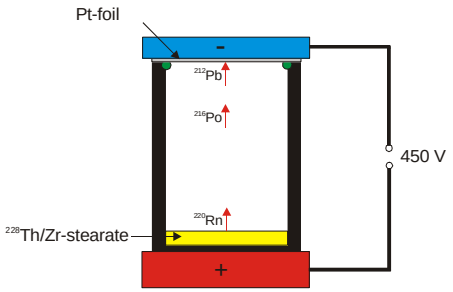

Figure 1: Schematic construction of a ^{228}Th / ^{220}Rn / ^{212}Pb - generator for the separation of carrier-free ^{212}Pb.

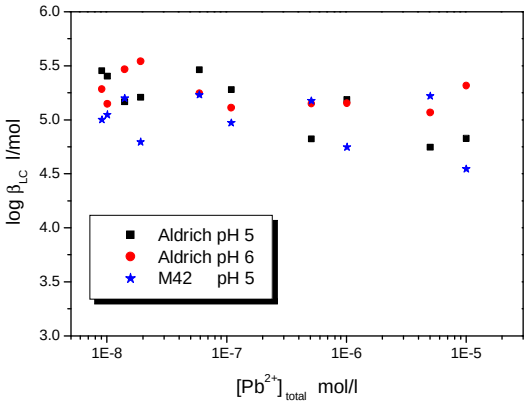

Figure 2: Dependence of the complexation constant log β_{LC} on the total Pb concentration; ^{212}Pb as radiotracer.

[1] S. Pompe et al., Radiochim. Acta **82**, 89 (1998)
[2] A. Mansel et al., GDCh-Jahrestagung (2001)
[3] A. Seibert et al., Radiochim. Acta **89**, 505 (2001)
[4] J. I. Kim et al., Radiochim. Acta **73**; 5 (1996)