

Limitation of the Ultrafiltration Method for the Determination of Complexation Constants of Pu(IV) with Humic Substances

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Humic substances (HS) form strong complexes with heavy metals like plutonium. This behaviour can lead to an increase of the migration of the elements.

The complexation constants of Pu(IV) with Aldrich humic acid were determined at pH-values from 1.8 to 3.0 for varying humic acid (HA) concentrations (0, 1.0, 10, and 25 mg/L) [1]. Due to the precipitation of HA at pH < 3 [2] and thus a possible co-precipitation of Pu with HA, the complex formation studies with Pu(IV) were extended to pH > 3 using the ultrafiltration method.

As a first step, the recovery of plutonium(IV) after ultrafiltration in the absence of humic acid was investigated, i.e., the amount of adsorbed Pu on the filter and/or vessel material was determined. Pu(IV) was produced electrochemically and the oxidation state was confirmed by UV/VIS spectroscopy. A concentration of 4.15×10^{-7} M Pu was used at different pH-values (1.8, 2.5, 3.0, 3.8, and 4.8) with 0.1 M MES (2N-Morpholinoethane sulfonic acid) as buffer and NaClO₄ to fix the ionic strength at 0.1 M. The pH-value of the Pu(IV) solution was adjusted with 0.1 M NaOH or 0.1 M HClO₄. The Pu solutions were ultrafiltered by using filters with different pore sizes (1, 3, 10 kDa) and the concentration of Pu in the filtrates was measured by liquid scintillation counting (LSC).

The percentage of plutonium recovery was calculated for the different pH-values (see Figure 1). The recovery is 85% at pH 1.8, 59% at pH 2.5, 48% at pH 3.0, 18% at pH 3.8, and 13% at pH 4.8. No differences were observed for the different filter pore sizes (1, 3, 10 kDa). Referring to the decreasing percentages of recovery for Pu(IV) at increasing pH, a determination of complexation constants with HS using the ultrafiltration method is not possible for higher pH-values without applying substantial corrections.

On the other hand, determining the complexation constants of Pu(IV) with HS for pH < 3 can lead to co-precipitation of Pu with HA due to the precipitation of HA at low pH-values yielding large uncertainties in the complexation constants [2].

Since fulvic acid is soluble in all pH ranges, it could be used for determining complexation constants at low pH-values, where adsorption effects on filter materials are almost negligible. However, ultrafiltration studies for Gorleben fulvic acid (FA) in absence and presence of different metal ions (Ca(II), La(III) and Zr(IV)) revealed that only 40 to 80% of FA was retained on the filter compared to 85% to 95% for HA [3]. Thus, the ultrafiltration method seems not be suitable to determine complexation constants of Pu(IV) with fulvic acid.

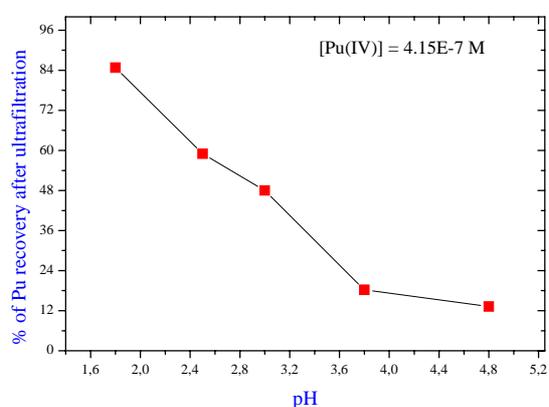


Figure 1: Percentage of plutonium recovery after ultrafiltration at varying pH-values (1 kDa filter pore size).

References:

- [1] N. L. Banik et al., Institut für Kernchemie, Universität Mainz, Annual Report, C10, (2003)
- [2] N. L. Banik et al., Institut für Kernchemie, Universität Mainz, Annual Report, (2004)
- [3] S. Bürger et al., Institut für Kernchemie, Universität Mainz, Annual Report, (2004)