Redox speciation of neptunium with CE-ICP-MS

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After a storage time of about 1000 years, the radiotoxicity of spent nuclear fuel will mainly be determined by long-lived isotopes of Pu and minor actinides, such as ^{237}Np ($T_{1/2}$ = 2.14×10^6 a). Hence, a good understanding of the geochemical properties of these elements is essential. Under environmental conditions, the migration of Np is predominantly affected by its oxidation state. Whereas Np(V) is easily soluble in aqueous phases, Np(IV) shows a strong tendency towards sorption onto various substrates. Since the neptunium concentrations expected in case of a leakage of a repository are below 10^{-10} mol×L^{-1}, sensitive techniques are required for studies on redox speciation of Np. Therefore, we have examined weather CE-ICP-MS is a suitable method for Np redox speciation at trace concentrations.

A homemade capillary electrophoresis (CE) setup was coupled on-line to an ICP-MS (7500ce, Agilent Technol., Santa Clara, CA, USA) in order to separate and quantify traces of Np(IV) and Np(V) in solution.

A mixture of both oxidation states was obtained by partial reduction of a Np(V) stock solution (c = 1.1×10^{-4} mol×L^{-1}) with hydroxylammonium chloride. The content of Np(IV) and Np(V) in this solution was checked by liquid-liquid extraction of Np(IV) with HDEHP and LSC measurements of the aqueous and organic phases. For the experiments with the CE-ICP-MS, the Np(IV, V) solution was diluted to total Np concentrations between 4×10^{-9} and 4×10^{-6} mol×L^{-1} with acetic acid (c = 1 mol×L^{-1}), which also served as CE background electrolyte. Since Np(IV) gets easily oxidized, the dilution was done immediately before injecting the samples onto the CE capillary in all cases.

The separation of the two Np oxidation states was carried out with fused silica capillaries (l = 80 cm, i.d. = 50 µm) at a voltage of 25 kV. During the separation, a pressure of 25 mbar was applied on the capillary to prevent it from clogging. The coupling of the CE with the ICP-MS was archived with a MiraMist CE nebulizer (Burgener Research, Mississauga, ON, Canada) and a Scott type spray chamber.

Under these conditions, a good separation of Np(IV) and Np(V) is possible (Fig. 1) within roughly 10 minutes. A limit of detection (threefold standard deviation of the blank) of 1×10^{-9} and 6×10^{-10} mol×L^{-1} for Np(IV) and Np(V), respectively, has been obtained. The increase in sensitivity of more than two orders of magnitude compared to previous experiments [1] can largely be attributed to the low flow nebulizer applied in our work.

A dilution series of the Np(IV, V) mixture showed a linear increase of both the Np(IV) and Np(V) peak areas with concentration without systematic deviations (Fig. 2). This behavior indicates that there is no significant loss of Np(IV) due to sorption on the sample vials or the capillary at low concentrations. Also, there is no rapid oxidation of Np(IV) traces if the sample solutions are handled accordingly. From our results, we conclude that CE-ICP-MS is well suited for the redox speciation of Np in the examined concentration range.

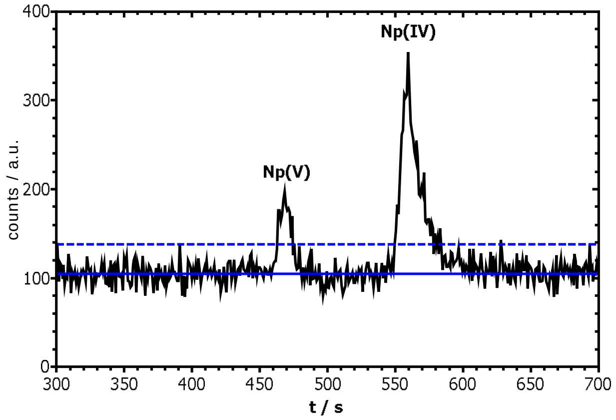

Figure 1: Electropherogram of a mixture of 9.2×10^{-10} mol×L^{-1} Np(V) and 3.1×10^{-9} mol×L^{-1} Np(IV). —— : Background, ----- : 3σ -background (LOD).

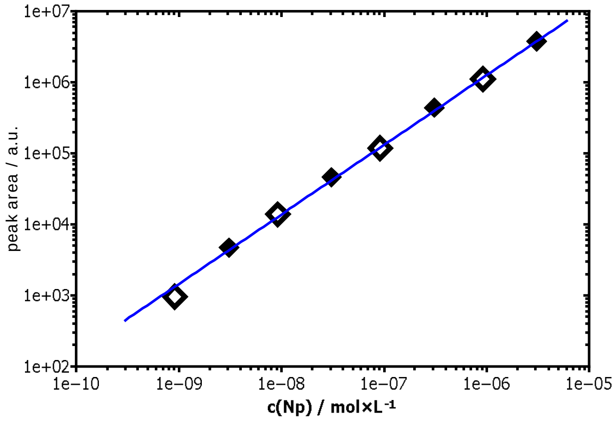

Figure 2: Linear increase of the peak area with concentration. Values for: ◆ Np(IV), ◇ Np(V)

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References

[1] B. Kuczewski et al., Anal. Chem. 75, 6769 (2003).