

Speciation of the oxidation states of plutonium in aqueous solutions by offline coupling capillary electrophoresis to resonance ionization mass spectrometry

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For the long term safety assessment of nuclear waste repositories or contaminated sites, the knowledge about the behavior of plutonium in geogenic systems is of great importance. The understanding of the physical and chemical processes responsible for the mobilization or immobilization of plutonium is required for the prediction of the migration behaviour of plutonium.

Plutonium can coexist in aqueous solutions in four different oxidation states, Pu(III) to Pu(VI). The speciation of plutonium oxidation states in solution is possible with various methods, mainly spectroscopic or laser based techniques, e.g., UV-visible spectroscopy, extended x-ray absorption fine structure (EXAFS), x-ray photoelectron spectroscopy (XPS), laser induced breakdown spectroscopy (LIBS) for colloids, or capillary electrophoresis (CE) coupled to ICP-MS. The detection limits of these speciation methods vary between 10^{-5} to 10^{-9} mol Pu/L. Therefore, the concentrations below the solubility limit of Pu(IV) (10^{-7} - 10^{-11} mol/L for pH > 4), expected in the far field of a nuclear repository site, is not accessible with these speciation methods. To fill this gap, the coupling of capillary electrophoresis (CE) to resonance ionization mass spectrometry (RIMS) for the speciation of plutonium oxidation states in solution at ultra trace concentrations has been developed.

The principle of coupling CE to RIMS is based on collecting fractions of the different oxidation states eluted from the capillary at different, but known retention times [1,4]. The CE system used is an improved version of the previously published homemade system [2]. By using a multiple resonant laser excitation and ionization of the element of interest, RIMS provides an excellent element and isotope selectivity and a detection limit of 10^6 - 10^7 atoms for the plutonium isotopes ^{238}Pu - ^{242}Pu , and ^{244}Pu [3], thus enabling speciation studies at ultra trace concentrations by coupling RIMS offline to CE.

The coupling of CE to RIMS was tested by determining the plutonium oxidation states of a mixture of Pu(IV), Pu(V), and Pu(VI) by CE-

ICP-MS at a plutonium concentration of ca. $4 \cdot 10^{-6}$ mol/L and by comparing the data with the determination by RIMS at a plutonium concentration of ca. $2.5 \cdot 10^{-7}$ mol/L after separation and fractionation by CE. Table 1 compares the measurements by CE-ICP-MS and by CE offline coupled to RIMS.

Table 1: Comparison between the determination of the oxidation states of plutonium by CE-ICP-MS (ca. $4 \cdot 10^{-6}$ mol/L plutonium) and by RIMS (ca. $2.5 \cdot 10^{-7}$ mol/L) after separation by CE in different fractions (CE-RIMS offline)

| | Pu(V+VI) [%] | Pu(IV) [%] |
|-----------------------------------|--------------|------------|
| CE-ICP-MS | 19.2(2.0) | 80.8(3.0) |
| CE offline coupled to RIMS | 15.2(5.0) | 84.8(5.0) |

The speciation of plutonium oxidation states by CE coupled offline to RIMS presented here is below the speciation limit of the CE-ICP-MS system used so far. The detection limit of RIMS enables to decrease the concentration of plutonium by 2 to 3 orders of magnitude compared to CE-ICP-MS. Thus, speciation of the oxidation states of plutonium at the ultra trace level of 10^{-9} to 10^{-10} mol/L appears to be possible [4].

An open question is the influence of cross contamination at concentrations below 10^{-7} mol/L Pu due to sorption of plutonium onto the inner wall of the capillary and desorption during subsequent CE separations with the same capillary. Hence further experiments are necessary.

Literature:

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