Contribution ID: **349**   Type: **Poster**

Analysis of the factors that may lead to misinterpretation of U(VI) complexes time-resolved laser-induced fluorescence spectroscopy data

Monday, 12 May 2014 17:15 (1h 30m)

The aqueous chemistry of Uranium(VI) determines its migration in geosphere under oxic conditions and the efficiency of some technological processes like in situ leach uranium mining, thus being extensively studied in geochemistry. Time-resolved laser-induced fluorescence spectroscopy (TRLIFS) is a powerful method that allows one to determine U(VI) speciation both in aqueous solutions and at mineral-water interfaces. TRLIFS makes use of the sensitivity of U(VI) complexes photophysical parameters (excited state lifetimes and positions of maxima in fluorescence emission spectra) sensitivity to its coordination. Because of high sensitivity and selectivity, this method is extensively used in investigation of various systems containing U(VI), including equilibrium constants determination and monitoring U(VI) speciation in drainage waters.

At the same time, the values of excited state lifetimes of, e.g. uranyl fluoride and sulfate complexes, obtained by different groups differ significantly. Moreover, even the question about the number of components required for fluorescence decay curves fitting is not clear: some researchers consider discreet lifetimes for different complexes, while others postulate a continuous dependency of lifetime on ligand concentration and interpret their data under the assumption of fast ligand exchange.

Here, we'll present the extensive study of the reasons that may lead to the discrepancy of photophysical parameters obtained for the same complexes. First, recently, we have demonstrated that the effect of excited states annihilation may influence the shape of fluorescence decay curves at high excitation intensities, thus leading misinterpretation of fluorescence decay rates. Second, different algorithms of fluorescence decay curves processing (the use of fixed lifetimes, global analysis etc.) may provide different values of complexes amplitudes and, consequently, equilibrium constants. Third, we'll demonstrate the influence of ionic strength of the solution on U(VI) complexes photophysical parameters and stoichiometry by the example of uranyl sulfate complexes.

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Session Classification: Poster Session - Separation Methods, Speciation

Track Classification: Separation Methods, Speciation