

Laser-induced Photoacoustic Spectroscopy for the Chemical Speciation of Pu(VI)

H.-R. Cho*, E. C. Jung, W. Cha, K. Song
Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute
1045 Daedeok-daero, Yuseong, Daejeon 305-353, Korea
hrcho@kaeri.re.kr

1. Introduction

Speciation of actinide in natural aquatic system is of great interest for the safety assessment of a nuclear waste disposal in deep geological system [1]. Actinide ions form complicate complexes with various ligands such as OH^- , CO_3^{2-} , and humic substances in groundwater. These complexes can enhance or reduce the migration of actinide elements. The direct speciation of these complexes in groundwater requires a highly sensitive and selective method which is capable to determine trace amount of actinides and to identify the different complexes without separation. Time-resolved laser-induced fluorescence spectroscopy (TRLFS) is a very suitable method for trace analysis (down to 10^{-9} M) of some actinides such as U(VI), Cm(III) and Am(III). For chemical speciation of actinides complexes which show no fluorescence feature such as U(IV), Pu(III-VI) and Np(IV/V) complexes, laser-induced photoacoustic spectroscopy (LPAS) was reported a possible sensitive spectroscopic technique (down to 10^{-6} M) [2-3].

In this work, a LPAS system using a tunable laser which can be tuned from 410 to 2400 nm was installed to investigate various actinide complexes. Optical parametric oscillator (OPO) technique makes it convenient to investigate various actinides absorbed in visible and near-IR wavelength ranges. In this work, LPAS was applied for the speciation of U(IV) and Pu(VI) ions in visible and near-IR wavelength range. Absorption of water in aqueous samples has influence on LPAS spectra of target ions over 600 nm in wavelength. Speciation sensitivity of μM concentration ranges for Pu(VI) were achieved.

2. Experimental

Figure 1 shows a schematic diagram of the LPAS system. An OPO pumped by a Q-switched Nd:YAG laser (OPOTEK Inc., Vibrant 355 II) was applied as a light source with a repetition rate of 10 Hz and a pulse duration of 5 ns. Laser pulse energy was measured by using an energy meter (J4-05, Coherent), amplified by a preamplifier (SR240A, Stanford Research System) and integrated by using boxcar averager (SR250, Stanford Research System). Measured photoacoustic signal was divided by the magnitude of laser pulse energy varied with wavelength. Two identical sample holders were designed for tight contact between piezoelectric transducer (PZT) detectors and quartz cells ($10 \times 10 \times 35$ mm³, Hellma). The laser beam passes through one cell containing the reference solution and the other containing the actinide ions. The output signals from

PZT detectors were amplified (Low-noise preamplifier, SR560, Stanford research system). For gated detection of photoacoustic signal, gated integrator (SR250, Stanford Research System) was applied. Integrated signals were digitized by a multifunction DAQ (NI PXI-6251, National Instruments) and recorded by using a home-made software based on LabVIEW (National Instruments).

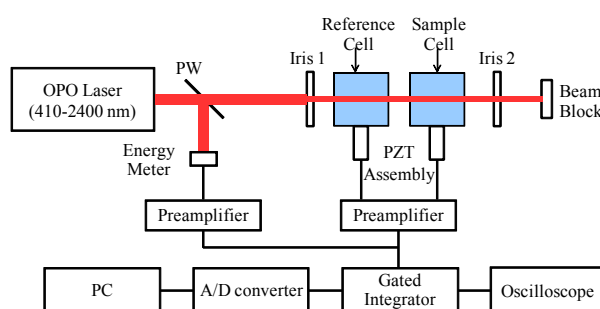


Figure 1. Experimental setup for LPAS measurements.

A U(VI) stock solution was prepared as described in a previous work [4] in 0.1 M HClO_4 . Concentration of the stock solution was 89.5 ± 0.15 mM determined by potentiometric titration with a standard dichromate solution based on Davies and Gray's method [5]. An aliquot of the U(VI) stock solution was acidified to pH 0 and reduced by electrolysis (Hg-Pt electrodes). The reduced solution was a mixture of U(III) and U(IV). U(III) was spontaneously oxidized to U(IV) due to its instability in an aqueous solution. The stock solution of U(IV) was kept in a glove box filled with Ar gas to prevent re-oxidation to U(VI). The concentration of U(IV) was 80.6 mM. U(IV) samples in the concentration range of 1×10^{-6} - 5×10^{-5} M at a pH range of 0-2 were prepared from the U(IV) stock solution.

A Pu(VI) stock solution (99.932% Pu-242) was prepared as described in previous work [6]. The concentrations of other oxidation states (Pu(III), Pu(IV), and Pu(V)) in the Pu(VI) stock solution were not detected by using a UV/Vis/NIR spectrophotometer (Cary 5, Varian). Pu(VI) samples in the concentration range of 1×10^{-6} - 5×10^{-5} M were prepared from the Pu(VI) stock solution.

3. Results and Discussion

Figure 2 shows LPAS spectrum of U(IV) free ion measured in a wavelength range from 520 to 700 nm. The laser pulse energy gradually decreased from 20 to 7 mJ with an increase of wavelength from 520 to 700 nm.

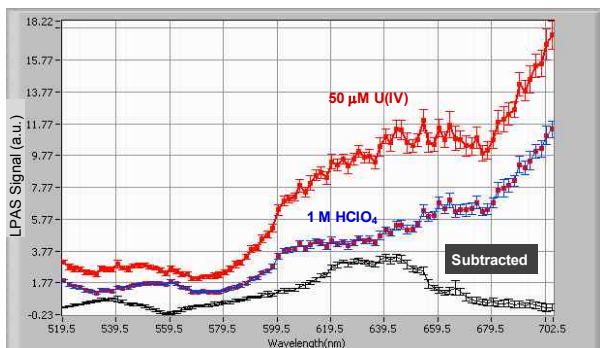


Figure 2. LPAS spectra of U(IV) free ion and background material (1 M HClO₄ in H₂O). The Black line indicates the LPAS spectrum of U sample solution with the subtraction of the signal of background material.

The magnitude of PZT signal was divided by the magnitude of pulse energy for every pulse. This signals were averaged 20 or 98 pulses at the fixed wavelength and presented as LPAS signal in Figure 2. The averaged signals were recorded in the wavelength range from 520 to 700 nm with a interval of 1 nm. The middle trace indicates LPAS spectrum of 1 M HClO₄ in H₂O solution. The increase of water absorption (background signal) from 520 to 700 nm in wavelength was consistent with reported data in literature [7]. The upper trace indicates LPAS signals obtained from U(IV) sample cell. It contained both the absorption of water and U(IV) free ions. When LPAS signal of sample cell was subtracted with that of reference cell, the real spectrum can be obtained as represented by the lower trace. The subtracted LPAS spectrum was consistent with absorption spectrum of U(IV) free ions measured by a UV-Vis spectrophotometer (data not shown).

Figure 3 shows LPAS spectrum of Pu(VI) free ion measured in a wavelength range from 815 to 845 nm. Although the absorption of water is dramatically increased in near-IR wavelength ranges, the LPAS spectrum of Pu(VI) in concentration of 10 μM shows a well known narrow absorption band of Pu(VI) at 831 nm. This spectrum shows the improved S/N ratio compared with that obtained from a conventional spectrophotometer. Red shifted absorption spectra of Pu(VI) hydrolysis species were investigated by LPAS. The characteristics of LPAS spectra will be discussed in comparison with the previous results [6] measured by a conventional spectrophotometer.

4. Conclusions

A LPAS system using an OPO laser pumped by Nd:YAG laser which can be tuned from 410 to 2400 nm were established for the chemical speciation of actinide in solutions. The absorption bands of actinide species appear in wide wavelength ranges. For example, Pu(III), (IV), Pu(V) and Pu(VI) absorb at 600, 470, 569 and 831 nm, respectively. With the aid of this system it is expected to conveniently investigate various actinide species, especially, redox-sensitive plutonium complexes.

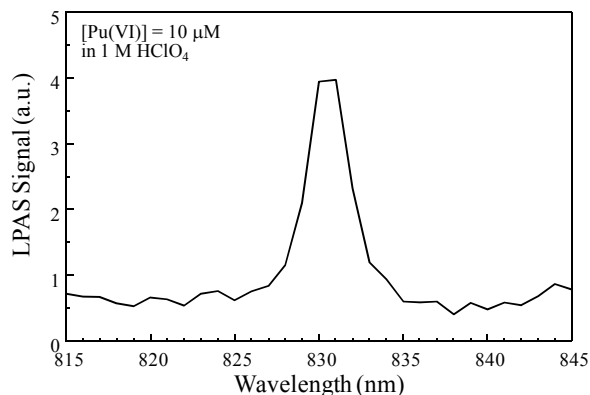


Figure 3. LPAS spectrum of PuO₂²⁺ ions corrected by background signal of 1 M HClO₄ in H₂O ([Pu]=10 μM).

Acknowledgement

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