

Speciation of U(VI) Using a 1.0-meter Liquid Waveguide Capillary Cell

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1. Introduction

The chemical behaviors of actinides are of great interest in the research field of the migration of water-soluble radionuclides. They form complexes with inorganic or organic ligands such as OH^- , CO_3^{2-} and humic substances, etc. in a groundwater. Therefore, an accurate determination of these different species will improve our understanding of their chemical reactions in natural aquatic systems [1]. To achieve this, non-invasive spectroscopic techniques with a high sensitivity are necessary.

In this paper we report on the absorption spectroscopic technique by using a 1.0-meter liquid waveguide capillary cell (LWCC) for the detection and quantification of UO_2^{2+} and its hydrolysis species. By varying the pH and uranium concentration at a fixed ionic strength, the identification of various species such as UO_2^{2+} and $(\text{UO}_2)_2(\text{OH})_2^{2+}$ has been performed. Because of the higher detection sensitivity of LWCC, we could investigate directly aqueous U species in concentration range of ppms.

2. Experimental

An experimental setup is shown in Figure 1. UV-Vis absorption spectra of aqueous uranium species were measured in the wavelength range of 200-500 nm. A LWCC (WPI) with an effective path length of 1.0-meter was used. It consists of a fused silica capillary coated by Teflon AF with an inner diameter of 0.5 mm. The sample volume of the LWCC is about 0.3 mL. Optical fibers with a core diameter of 0.6 mm were connected to a UV-Vis spectrometer (Cary 3E, Varian). Compared to a conventional absorption spectroscopy by using a standard 1.0-cm cuvette (Hellma), the signal obtained from the LWCC is simply enhanced by extending the optical path length.

A uranium stock solution was prepared with natural ^{238}U purified by a H_2O_2 -precipitation [2] in 6 M HClO_4 . U(VI) samples in the concentration range of 10^{-2} - 10^{-6} M with a pH range of 1.0-6.0 were prepared from a stock solution at room temperature being equilibrated with air. In general, U(VI) carbonate complexes are not formed under a 0.03% CO_2 condition (air) at below pH 7. Thus, U(VI) carbonate complexes can be ignored in the present experimental conditions. All the samples were appropriately diluted with 0.1 M HClO_4 (analysis grade, Merck), 0.1 M NaOH (Titrisol, Merck) and 0.1 M NaClO_4 solutions to maintain a 0.1 M ionic strength. For a purification, $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (analysis grade,

Merck) was carefully recrystallized and then diluted in ultra-pure water (Millipore). The pH measurement was carried out by a Ross-type combination glass electrode calibrated with several pH buffer solutions. The uranium concentration of stock solution was determined by using a kinetic phosphorescence analyzer (KPA-11, Hemchek).

3. Results and Discussions

UV-Vis absorption spectrum of UO_2^{2+} is characterized by a broad and weak transition with a maximum peak at 413.8 nm [3]. The molar absorption coefficients ranging from $7.8 \text{ M}^{-1}\text{cm}^{-1}$ in 0.014 M HClO_4 [3] to $9.7 \text{ M}^{-1}\text{cm}^{-1}$ in 0.1 M HClO_4 [4] were reported.

Figure 2(a) illustrates the representative examples of the absorption spectra of U(VI) with the concentration of 10^{-3} M at pH 1. The black and blue lines mean the spectra measured by using a standard 1.0-cm quartz cuvette and 1.0-m LWCC, respectively. For the case of a black line, the measured molar absorption coefficient is $8.2 \text{ M}^{-1}\text{cm}^{-1}$ which agrees with previously reported values. Furthermore, we confirm that several peak positions also agree well with reported wavelengths of UO_2^{2+} ion. Thus, we conclude that the U(VI) species being present in this condition is only the UO_2^{2+} ion. Absorption spectrum designated as the blue line obtained from a 1.0-m LWCC shows a 100 times higher absorbance when compared to the spectrum designated as a black line. The estimated detection limits of the UO_2^{2+} species is 4×10^{-5} M with a 3σ absorbance of 3×10^{-4} by using a conventional 1.0-cm quartz cell. In case of a measurement by using a 1.0-m LWCC, its sensitivity shows more than tens times higher than a 1.0-cm quartz cell. The enhanced noise in the extended beam path length is presumably the reason for the sensitivity increment of less than 100.

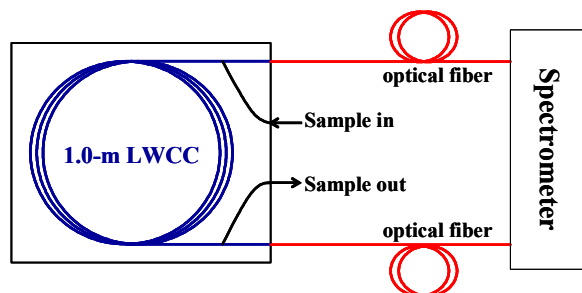


Figure 1. Overview of LWCC experimental setup. A 1.0-m LWCC is coupled with a UV/Vis absorption spectrometer by optical fibers (core size of 0.6 mm).

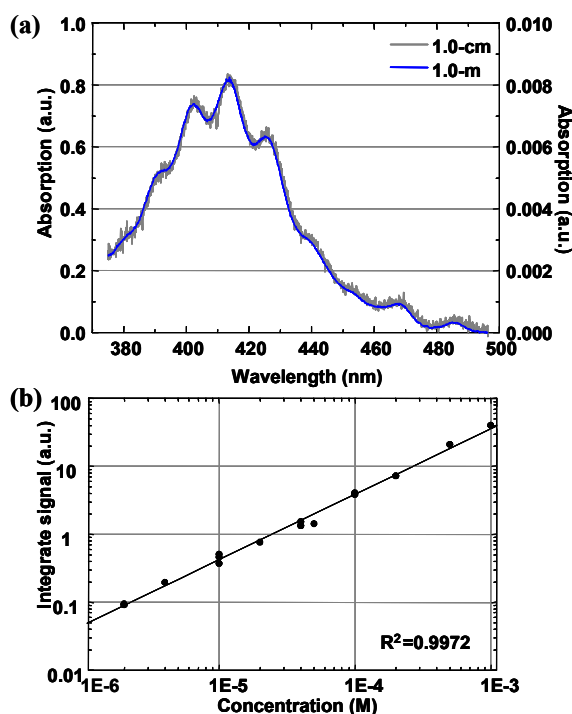


Figure 2. (a) Absorption spectra of 10^{-3} M UO_2^{2+} at pH 1 in 0.1M HClO_4 . The black and blue lines mean the spectra measured using standard 1.0-cm quartz cell and 1.0-m LWCC, respectively. (b) Calibration curve for the concentration measurement of UO_2^{2+} at pH 1 in 0.1M HClO_4 by using a 1.0-m LWCC.

For a calibration purpose several absorption spectra were measured by using LWCC in the concentration range from 10^{-6} M to 10^{-3} M at pH 1 and the results are shown in Fig. 2(b). The symbols indicate the integrated absorbance in the wavelength range from 375 nm to 500 nm. The calibration curve designated as a solid line illustrates a precise linear dependency with a regression coefficient better than 0.99. For a more accurate calibration, the calibration curve is obtained from an integrated absorbance corresponding to the total area of the spectrum, since the absorption peak is so broad due to a poor spectral resolution.

Figure 3 shows the absorption spectra for 10^{-3} M samples at several pH values measured by using a 1.0-cm quartz cell. It can be seen that at from pH 1.0 to 3.3 the spectra are not changed and are those of a UO_2^{2+} ion, as shown in Fig. 2(a). Above pH values higher than 3.3, a shift in the peak position and an increase of the absorbance are observed. These characteristic features are due to the formation of hydrolysis species. Meinrath reported on the strong increase in an absorbance with a hydrolysis at a relatively high concentration (about 5×10^{-3} M) and he verified the existence of polynuclear species such as $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$ [4]. When the measured spectra are deconvoluted with the reference spectra obtained by Meinrath, the sample at pH 4.3 contains about 10% of $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and 90% of UO_2^{2+} . The other spectroscopic measurement such as a fluorescence spectroscopy is in progress for a more detailed analysis of the different species.

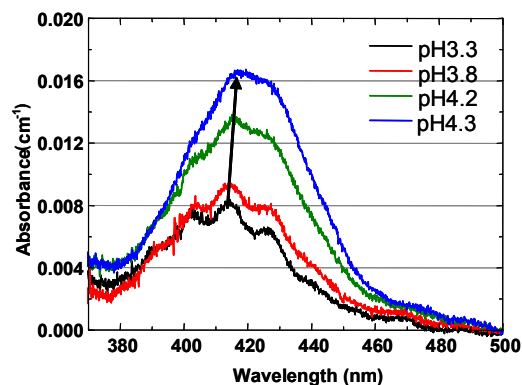


Figure 3. Absorption spectra of 10^{-3} M U(VI) at various pHs; pH 3.3 (black line), pH 3.8 (red line), pH 4.2 (olive line) and pH 4.3 (blue line).

4. Conclusions

In the present study, the absorption spectra of aqueous uranium species were measured by using the 1.0-m LWCC coupled with a UV-Vis spectrometer. Due to the extended beam path length, the detection sensitivity for the free uranyl ion was enhanced by more than ten times when compared to the conventional absorption spectra measured by using a standard 1.0-cm quartz cuvette. The detection limit of the free uranyl ion decreases to a few ppm. It is expected that a concentration lower than a few ppm can be detected with the 1.0-m LWCC for the hydrolysis species, because these species show an increasing absorbance of more than a ten times. Further spectroscopic measurements will be presented at higher pH values with much lower concentration ranges.

REFERENCES

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