

## Concentration Measurement of Uranium Dissolved in Seawater using Laser-induced Fluorescence Spectroscopy

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### 1. Introduction

The concentration of uranium in seawater is approximately 3.3 parts per billion (ppb), necessitating an analytical method capable of detecting trace amounts of uranium. Seawater contains high concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$  ions, which are  $10^5$  to  $10^7$  times greater than uranium. This high background ion concentration can distort analysis results due to matrix effects in inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Consequently, samples are often diluted significantly, or background ions are removed through chemical pretreatment using ion exchange resin. Spectroscopic methods employing laser-induced fluorescence (LIF) have been widely utilized to analyze trace amounts of uranium(VI) in groundwater and freshwater [1,2,3]. However, the presence of various ions and organic substances in seawater often quenches uranium fluorescence, posing challenges for accurate concentration measurements.

This study introduces a method for quantitatively analyzing uranium in seawater using laser-induced fluorescence spectroscopy (LIF), a highly sensitive analytical technique. The uranium concentration in actual seawater environmental samples was determined using this method. Additionally, by analyzing seawater samples with low uranium concentration, the limit of detection (LOD) for uranium in seawater samples using this technique was calculated.

### 2. Materials and Methods

#### 2.1. Materials

The experiment utilized a 10,000  $\mu\text{g/mL}$  Uranium ICP standard solution (CGU10, Inorganic Ventures, USA). Deionized water (18.2 M $\Omega$ ), prepared using a water purification system (Milli-Q/Rios, Millipore), was used for solution preparation, dilution, and washing. Sea salt (S9883, Sigma-Aldrich) was also employed to make artificial seawater. Before being used, the sea salt was dissolved in distilled water and filtered through glass microfiber filters with a 1.0  $\mu\text{m}$  particle retention rating (Whatman, Grade GF/B), and the filtered solution was evaporated to obtain sea salt devoid of insoluble impurities. 70% nitric acid (225711, 99.999% trace metals basis, Sigma-Aldrich) and 85% phosphoric acid

(345245, 99.99% trace metals basis, Sigma-Aldrich) were utilized in the experiment.

All glass vials designated for storing the solution were scintillation glass vials (WH.986546, Wheaton). Four window quartz cuvettes (111-QS, Hellma Analytics) were utilized for laser-induced fluorescence spectroscopy. Before their use, all glass vials and quartz cuvettes underwent a cleaning process to minimize contamination. The cleaning process involved washing them with deionized water, immersing them in 2% nitric acid for 24 hours, washing them with deionized water, and finally drying them on a clean bench. The 2% nitric acid used in the cleaning process was also manufactured by diluting 70% nitric acid (99.999% purity) with deionized water.

#### 2.2. Methodology

Fig. 1 shows a schematic diagram of the laser-induced fluorescence spectroscopy (LIF) system. The system was constructed using an Nd:YAG laser (Brilliant B, Quantel). This Brilliant B Nd:YAG laser with a wavelength of 1064 nm has a laser pulse width (full width at half maximum, FWHM) of 5 ns and a repetition rate of 10 Hz. The fourth harmonic laser beam with a wavelength of 266 nm was generated using fourth harmonic generators to obtain the uranium fluorescence spectrum. The fluorescence signals were obtained with a Czerny-Turner spectrometer (SR-303i-A, Andor Technology) paired with an ICCD camera (DH734-18F-C3, Andor Technology). The spectrometer performed wavelength calibration using a mercury-argon calibration lamp.

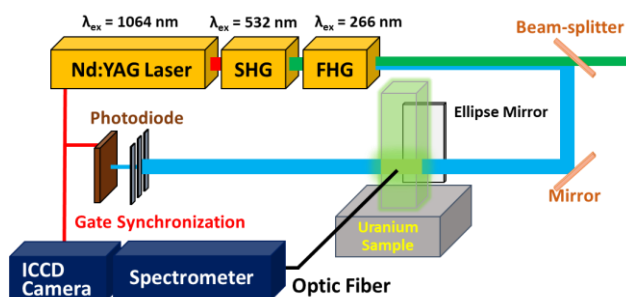


Fig. 1. Schematic diagram of the laser-induced fluorescence spectroscopy (LIF) system.

The laser beam power measurements were performed using a thermopile energy detector (UP19K-30H-VR-D0)

and an energy meter (Gentec-EO Maestro). The laser beam power at 266 nm was measured 20 minutes after turning on the flashlamp and Q-switch. By setting the Q-switch delay time to 275  $\mu$ s and measuring a sample rate of 10 samples/s for 10 minutes, the average laser beam power was 106.53 mW, the standard deviation was 1.838 mW, and the average pulse energy was 10.653 mJ.

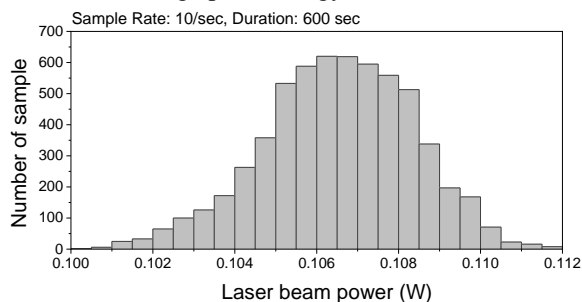


Fig. 2. Histogram of laser beam power measurement data, with an average laser beam power of 106.53 mW.

### 2.3. Sample preparation

The presence of halide ions ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ) in seawater is known to induce a quenching effect on uranium fluorescence [4]. Rathore et al. [5] investigated this phenomenon by conducting laser-induced fluorescence measurements on uranium concentrate. Their study revealed that the addition of nitric acid to an aqueous solution containing halide ions, followed by heating, effectively removes these halides.

To eliminate halide ions from seawater samples, the following procedures were conducted: 5 mL of seawater sample and 3 mL of 70% high-purity nitric acid were added to a cleaned 20 mL glass vial. The solution was thoroughly stirred and then dried in a ventilated oven set at 120 degrees Celsius. Once the sample was completely dried, 4 mL of 12.5% phosphoric acid and 6 mL of deionized water were added to the vial, ensuring thorough mixing. Subsequently, a portion of the solution prepared in this manner was transferred to a quartz cuvette for measuring uranium fluorescence.

### 2.4. Data processing

The data processing of the uranium fluorescence spectrum involved noise removal using either Savitzky–Golay (S-G) smoothing or Fast Fourier Transform (FFT) smoothing techniques. Subsequently, the area of the normalized peak at 517 nm was utilized for quantitative analysis of uranium and for generating calibration curves.

## 3. Result and Discussion

Before conducting quantitative analysis of uranium, time-resolved laser fluorescence spectroscopy (TRLFS) was performed to verify the complexation of phosphate ions with the uranyl ions. Fig. 3 presents the TRLFS data for a seawater sample spiked with 1.0 ppm uranium. The

calculated fluorescence lifetime of uranium in the phosphate medium was 135.7  $\mu$ s, a value consistent with the fluorescence lifetimes typically observed for U(VI)–phosphate complexes [6,7].

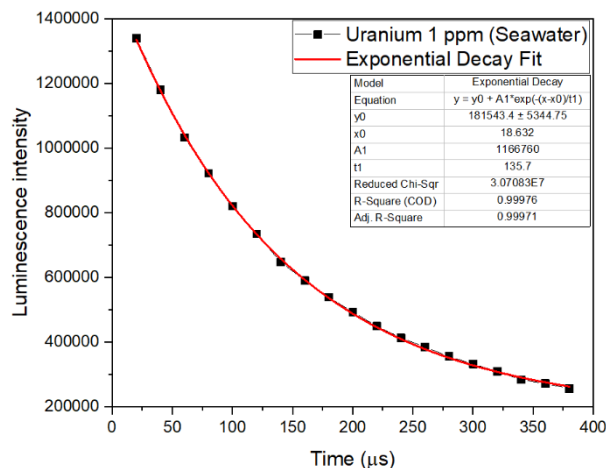


Fig. 3. Time-resolved laser fluorescence spectroscopy (TRLFS) data of seawater spiked with 1 ppm uranium. Fluorescence lifetime is 135.7  $\mu$ s. (Accumulation 200, gate delay 0.2  $\mu$ s, gate width 5  $\mu$ s, step 20  $\mu$ s, number of series 20.)

Fig. 4. shows laser-induced fluorescence spectroscopy (LIF) data of synthetic seawater added with 0 ppb, 1 ppb, and 5 ppb of uranium and seawater sample collected from the sea in Gampo-eup, Gyeongju-si on February 20, 2024.

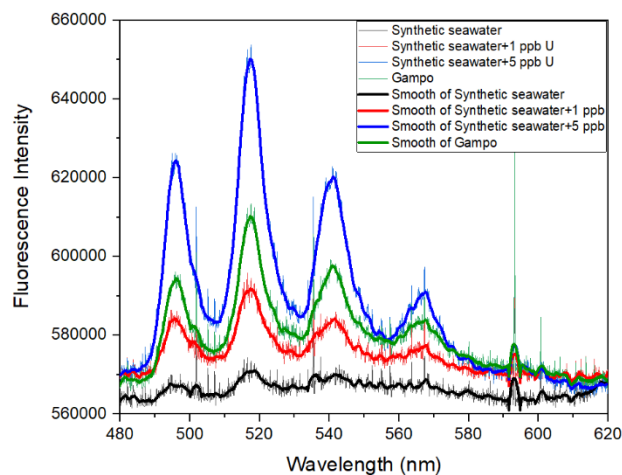


Fig. 4. Laser-induced fluorescence spectroscopy (LIF) data of seawater samples and synthetic seawater doped with 0 ppb, 1 ppb, and 5 ppb of uranium.

Fig. 5 shows the calibration curve derived from synthetic seawater standards to which uranium was added in concentrations ranging from 0 ppb to 10 ppb for calibration. By extrapolating the uranium fluorescence intensity at 517 nm using the calibration curve established in artificial, it was determined that artificial seawater prepared using purified sea salt (S9883, Sigma-Aldrich) had a uranium concentration of 1.08 ppb.

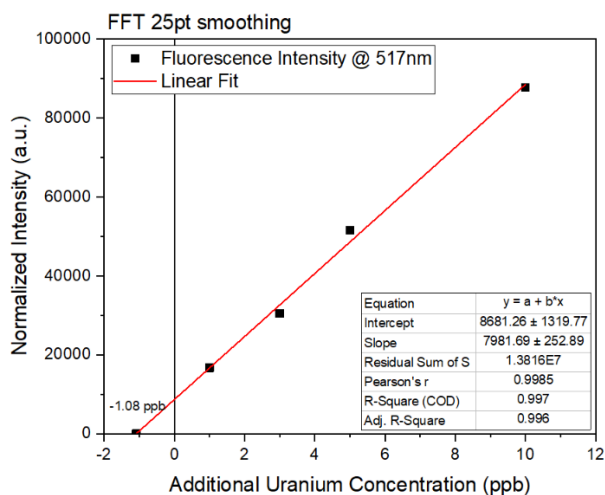


Fig. 5. Calibration curve of uranium standard solution prepared in seawater condition. (35 g/L of sea salts)

Considering the background uranium concentration in the calibration solution, the concentration of seawater samples collected from Gampo-eup was calculated. The seawater samples from Gampo-eup were measured three times using the same method, resulting in a concentration of  $2.89 \pm 0.191$  ppb.

$$(1) LOD_{3\sigma} = \frac{3 \times \sigma}{\text{slope}} = 0.4960 \text{ (ppb)}$$

Based on the calibration curve obtained in Fig. 5, the limit of detection is as shown in Equation 1.

#### 4. Conclusion

Uranium in seawater samples was quantitatively analyzed using laser-induced fluorescence spectroscopy (LIF). In this study, nitric acid was added to seawater samples and subsequently dried to eliminate halide ions, including  $\text{Cl}^-$  ions known to quench uranium fluorescence. Quantitative analysis of uranium concentration at the parts per billion (ppb) level was achieved in a phosphoric acid medium, which enhanced the uranium fluorescence intensity.

The limit of detection (LOD) for uranium was determined to be 0.496 ppb in uranium fluorescence measurements using sea salt containing a lower concentration of uranium (1.08 ppb) compared to seawater (3.3 ppb). With this detection limit lower than the typical concentration of uranium in seawater, it is anticipated that this method can be effectively employed in research involving seawater uranium adsorbents, where precise measurement of uranium concentrations lower than 3.3 ppb is crucial.

Furthermore, the 266nm laser used in the study delivers 10.653 mJ of energy per pulse, suggesting considerable potential for improving the limit of detection by employing even more powerful laser pulses.

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