Uranium determination in groundwater using laser spectroscopy

Abstract: The aim of this work is to review the laser-based analytical techniques for the quantitative determination of uranium in aqueous solutions. Among the various types of laser-based analytical techniques, two different spectroscopic techniques based on the measurement of laser-induced luminescence of hexavalent uranium ions [U(VI)] in groundwater are reviewed in detail. In the first technique, called time-resolved laser fluorescence spectroscopy, the time-resolved laser-induced luminescence intensities of U(VI) as a function of uranium concentration are measured to obtain the calibration curve. In the second technique, which is based on the simultaneous measurement of the U(VI) luminescence and Raman scattering of water, the calibration curve is obtained by measuring the ratio of the luminescence intensity of U(VI) to the Raman scattering intensity of water for the quantitative determination of uranium. A limit of detection of 0.03 μg/l was achieved at an excitation wavelength of 266 nm using these laser spectroscopic techniques. The results determined using these techniques are in good agreement with the results determined by inductively coupled plasma mass spectrometry (ICPMS). Thus, these laser-based analytical techniques will be useful to personnel requiring a rapid determination of uranium before the shipment of samples to an accredited laboratory, where relatively intricate and expensive apparatuses, such as ICPMS and radiochemical spectrometry, are used.

Keywords: groundwater; hexavalent uranium ions; laser spectroscopy; luminescence; uranium determination.

Introduction

Groundwater is used as drinking and agricultural water in a number of nations. The quantitative determination of uranium in groundwater is important for public health, because ingested uranium can cause both chemical and radiological toxicities (WHO 2011). The highest level of contamination that is allowed in drinking water is defined as the maximum contaminant level (MCL), and the U.S. Environmental Protection Agency (U.S. EPA) defines the MCL as 30 μg/l for uranium (U.S. EPA 2009). The Ministry of the Environment in the Republic of Korea decided that a quantitative analysis of uranium should be performed in 2014 for all waterworks using groundwater as raw water.

The principal source of uranium in the natural environment is leaching from natural deposits, and the concentration of uranium can be increased by the release of uranium from industrial processes, such as uranium mining and milling activities (WHO 2011). Furthermore, various aqueous solutions containing a high concentration of uranium are used in the nuclear fuel cycle related to the operation of nuclear power plants. When these solutions are transported by surface water and groundwater into the environment, both the chemical speciation and quantitative determination of uranium in these waters are essential for understanding the migration of radionuclides (Kim 2006). Research on the migration of radionuclides is of great importance for the safety assessment of nuclear waste disposal.

Inductively coupled plasma mass spectrometry (ICPMS) (U.S. EPA 1994, Pruszkowski and Bosnak 2012), radiochemical spectrometry (ASTM 2009a,b, 2013a), X-ray fluorescence (XRF; ASTM 2009c), and pulsed-laser phosphorimetry (ASTM 2013b) are the representative techniques for the quantitative determination of uranium. ICPMS is the most sensitive, accurate, and precise technique for the quantitative determination of uranium, but the high cost of the instrument and its complicated operation do not permit its use in most laboratories. In general, a minimum of 6 months of experience with commercial ICPMS instrumentation is recommended (U.S. EPA 1994). Radiochemical spectrometry, known as high-resolution liquid scintillation spectrometry and α-spectrometry,
covers the determination of α-particle-emitting isotopes of uranium in water by means of chemical separation and an analysis of the α-energy spectrum. In these techniques, sample preparation involves a time-consuming procedure to isolate uranium isotopes using chemical separation. XRF is an easy and rapid technique for the determination of uranium; however, its high limit of detection (LOD) is sometimes noted as a drawback.

Pulsed-laser phosphorimetry is a type of time-resolved laser fluorescence spectroscopy (TRLFS) (Decambox et al. 1991, Brina and Miller 1992, 1993). TRLFS is a sensitive and selective analytical technique with a low LOD and a large dynamic range, especially for hexavalent uranium ions [U(VI)] dissolved in aqueous solutions (Moulin et al. 1993, 1995, 1996, 1998). A U(VI) compound emits a characteristic green light (luminescence) with excitation by ultraviolet (UV) and blue wavelength radiation. The enhancement of the luminescence intensity can be accomplished by complexing uranyl ions (UO₂²⁻) with inorganic ligands, such as phosphate ions (PO₄³⁻), which yield a phosphorescence lifetime of a few hundred microseconds for U(VI) complex (Geipel 2006, Kumar et al. 2008). A commercially available instrument, called a kinetic phosphorescence analyzer (KPA), is widely used around the world and provides an analytical range from 0.01 μg/l to 5 μg/l (KPA-a 2009, Moore and Williams 1992).

A very simple analytical technique using laser-induced luminescence spectroscopy was recently developed in our laboratory (Cho et al. 2013, Jung and Cho 2014). This technique is based on the simultaneous measurement of the luminescence of U(VI) and Raman scattering of water and is quite different from pulsed-laser phosphorimetry, because it uses a calibration curve obtained by measuring the ratio of the luminescence intensity of U(VI) to the Raman scattering intensity of water for the quantitative determination of uranium (hereafter called ratiometric technique in this manuscript). Only a pulsed laser can be used to analyze the time-resolved luminescence in pulsed-laser phosphorimetry, whereas both pulsed and continuous wave (CW) lasers can be used in the ratiometric technique. In this paper, the characteristic features of these laser-based spectroscopic techniques (TRLFS and the ratiometric technique) that are relevant to the quantitative determination of total uranium in groundwater are reviewed in detail.

### Pretreatment of groundwater sample

The groundwater samples used in this experiment were collected from granite rocks located at the Korea Atomic Energy Research Institute (KAERI) Underground Research Tunnel (KURT) constructed in the research area of the KAERI in Daejeon, Republic of Korea. The flow rate for sampling was less than 0.4 l/min. Precipitates in the water samples were filtered out using a membrane filter with a pore size of 0.45 μm (Millipak 40; Millipore Co.). The sampled groundwater was a NaHCO₃-type alkaline solution with a low ionic strength of approximately 1.8–2.3 mM. Table 1 summarizes the sampling depth, solution pH, concentrations of dissolved organic carbon (DOC), and uranium contained in each groundwater sample. The concentration of uranium listed in Table 1 (column 5) was determined by ICPMS (Spectro MS, Spectro Analytical Instruments GmbH, Kleve, Germany) operated in an accredited laboratory of the KAERI. The concentration of uranium determined using laser-based spectroscopic techniques are compared with the values listed in Table 1.

Sample pretreatment must be performed carefully for determining trace amounts of uranium. When the sample contains undissolved uranium in the form of particulates, it can be dissolved by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made up to volume, mixed, and then filtered before analysis. When groundwater contains inorganic compounds, which may interrupt the determination of uranium by acting as reactants, absorbers, and quenchers (Sowder et al. 1998), stricter control of elemental composition is a prerequisite for laser-based spectroscopic analysis of uranium. The concentrations of metal cations, such as Na⁺ and Mg²⁺, in the sampled groundwater are below 25 mg/l; thus, these metal cations do not affect the measurement of trace uranium concentrations (Sowder et al. 1998). The quenching effect can be minimized by simple dilution of samples with appropriate chemicals such as nitric acid or the addition of strong luminescence-enhancing reagents. Phosphoric acid and polyphosphates are representative reagents that enhance the luminescence intensity of uranium by forming stable complexes with uranium (Kenney-Wallace et al. 1981, Zook et al. 1981, Geipel 2006, Kumar et al. 2008, ASTM 2013b).

### Table 1  Concentrations of DOC and uranium (²³⁸U) in the groundwater samples taken from the KURT. The concentration of ²³⁸U was determined by an ICPMS instrument operated in the accredited KAERI laboratory.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Depth (m)</th>
<th>pH</th>
<th>DOC (mg/l)</th>
<th>²³⁸U (μg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW1</td>
<td>41.7–59.7</td>
<td>8.4</td>
<td>0.386</td>
<td>36.7±0.2</td>
</tr>
<tr>
<td>GW2</td>
<td>229.7–245.7</td>
<td>8.3</td>
<td>1.626</td>
<td>5.8±0.4</td>
</tr>
<tr>
<td>GW3</td>
<td>246.7–299.7</td>
<td>8.5</td>
<td>0.384</td>
<td>3.5±0.1</td>
</tr>
</tbody>
</table>
In addition, the luminescence of natural organic matter (NOM) in groundwater also interrupts the precise determination of uranium due to the spectral overlap in the luminescence between NOM and uranium (Zook et al. 1981, ASTM 2013b). Figure 1 shows the representative data of time-resolved laser-induced luminescence spectra for the raw groundwater samples listed in Table 1. The experimental setup for measuring the time-resolved laser-induced luminescence spectrum will be described in detail in the next section. The peaks in Figure 1 (denoted by Arabic numerals) suggest that the uranium species exists in the form of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (aq.) in raw groundwater containing carbonate and calcium ions in alkaline pH conditions (Bernhard et al. 1998, Lee and Yun 2013). The broad plateaus that appeared for all samples in Figure 1 correspond to the luminescence spectra of NOM. The luminescence intensity of the plateau for the GW2 sample is stronger than the intensities of samples GW1 and GW3 because of the high concentration of DOC, as shown in Table 1 (column 4). It is generally accepted that NOM is usually represented by the measurement of DOC (Mattilainen et al. 2011). Although the concentrations of DOC for samples GW1 and GW3 are similar, the luminescence intensity of the plateau for the GW1 is weaker than that of GW3. This effect can be understood in terms of the different uranium concentrations for samples GW1 and GW3 due to the formation of nonluminescent complexes composed of organic ligands and uranium (Sowder et al. 1998).

In this work, the pretreatment of groundwater samples is focused on the removal of NOM to avoid NOM luminescence in the determination of uranium. The wet oxidation method used as part of the standard method for the quantitative analysis of total organic carbon (Clesceri et al. 1998) was used to remove the NOM in the groundwater samples. Because the standard method was developed to determine the carbon concentration, it was modified slightly for the purpose of this study (removal of NOM only). Thus, the collection and analysis of the resultant carbon dioxide during wet oxidation was omitted. The first step is to mix 10 mL of the groundwater sample and 0.2 g of potassium persulfate ($0.074 \text{ M } \text{K}_2\text{S}_2\text{O}_8$) in a glass vial as guided in the standard method (Clesceri et al. 1998). The vial was placed on a hot plate and mildly heated for approximately 2 h to dryness. The boiling of the sample solution was avoided at this step. $\text{K}_2\text{S}_2\text{O}_8$ slowly decomposes into potassium sulfate ($\text{K}_2\text{SO}_4$) and sulfuric acid ($\text{H}_2\text{SO}_4$) while being heated. After the sample is dried, 10 mL of distilled water were added to the sample; then, the sample was heated to dryness repeatedly until the absorbance of $\text{K}_2\text{S}_2\text{O}_8$ in the UV wavelength region decreased sufficiently to be comparable with that of a mixed sulfate solution ($0.074 \text{ M } \text{K}_2\text{SO}_4$ and $0.074 \text{ M } \text{H}_2\text{SO}_4$).

Figure 2 (solid lines) shows the absorption spectra of $\text{K}_2\text{SO}_4$ and mixed sulfate solutions. These spectra were measured with a UV-visible spectrophotometer (CARY 3; Varian, Melbourne, Australia). Very strong absorption was observed in the wavelength range below 300 nm for the $\text{K}_2\text{S}_2\text{O}_8$ solution, whereas this strong absorption was not observed for the mixed sulfate solution. Figure 2 (dotted lines) shows the decrease in absorption for the $\text{K}_2\text{SO}_4$ solution with repeated heating. The absorbance of the $\text{K}_2\text{S}_2\text{O}_8$ solution becomes similar to that of the mixed sulfate solution with three times repeated heating. Finally, reference solutions containing different uranium concentrations ranging from 1 to 50 $\mu$g/l in a mixed sulfate solution were prepared to obtain the calibration curve. The

![Figure 1](image1.png)  
**Figure 1** Time-resolved luminescence spectra for the raw groundwater samples listed in Table 1. The spectra were measured at a gate-delay time of 80 ns and gate width of 100 ns with the gated integrator and boxcar averager system described in Figure 3.

![Figure 2](image2.png)  
**Figure 2** Solid lines represent the absorption spectra for $\text{K}_2\text{SO}_4$ ($0.074 \text{ M}$) and mixed sulfate ($0.074 \text{ M } \text{K}_2\text{SO}_4+0.074 \text{ M } \text{H}_2\text{SO}_4$) solutions, whereas dotted lines represent the decrease of the absorbance of $\text{K}_2\text{SO}_4$ solution with repeated heating. $\text{K}_2\text{S}_2\text{O}_8$ decomposes into the $\text{K}_2\text{SO}_4$ and $\text{H}_2\text{SO}_4$ while being heated.
luminescence characteristics (peak wavelengths and lifetime) of the reference solutions are identical to those of groundwater samples pretreated with the K$_2$S$_2$O$_8$ solution, as shown in the following figures.

**Time-resolved laser fluorescence spectroscopy**

TRLFS is based on the selective excitation of a fluorophore in the ground state combined with the selective measurement of the time-resolved luminescence from the excited state. TRLFS enables highly sensitive and selective analysis of uranium, because the U(VI) species exhibit strong luminescence with irradiation by a laser beam (Brina and Miller 1992, 1993). Moreover, the chemical speciation of U(VI) complexes at trace-level concentrations can also be performed by analyzing the combined information on the luminescence spectrum with the luminescence lifetime, which depends on the nature of the ligands in aqueous solutions (Moulin et al. 1995, 1996, 1998). The state-of-the-art performances of TRLFS for the chemical speciation of actinides and determination of their concentrations were reported in recent review papers (Billard and Geipel 2008, Collins et al. 2011, Altmair et al. 2013, Geckeis et al. 2013, Panak and Geist 2013). The chemical speciation of trivalent curium and americium can be performed using TRLFS (Wimmer et al. 1992, Kim et al. 1994, Kimura and Choppin 1994, Panak et al. 1995, Runde et al. 2000, Cernochova et al. 2005, Stumpf et al. 2006, Barkleit et al. 2011).

Figure 3 shows a schematic diagram of the TRLFS experimental setup. A pulsed Nd:YAG laser (Minilite; Continuum, Santa Clara, CA, USA) beam at 266 nm was used as the excitation light source. The laser operated at a repetition rate of 10 Hz with an average pulse energy of 1 mJ. A part of the laser beam was reflected onto a photodiode (818 BB-21; Newport) by a beam splitter to generate the trigger signal for the gated integrator and oscilloscope. The laser beam passed through the sample cell (111-QS; Hellma Analytics), which was located inside a dark box to avoid ambient light. The luminescence perpendicular to the propagating direction of the laser beam was delivered to the entrance slit of the Czerny-Turner-type monochromator (iHR320; Horiba Jobin Yvon, Edison, NJ, USA) using an optical fiber bundle (cross-section of 2×8 mm², 345 fibers). Holographic grating (1200 grooves/mm) was installed inside the monochromator. The luminescence was recorded using a photomultiplier tube (PMT; R928; Hamamatsu Photonics, Iwata, Japan), and the signal measured by the PMT was electrically amplified by an amplifier (SR445A; Stanford Research Systems, Sunnyvale, USA). The waveform of the luminescence signal was measured using a digital oscilloscope (DPO 4102B; Tektronix). A gated integrator (SR250; Stanford Research Systems) and a boxcar averager (SR280; Stanford Research Systems) were used to measure the luminescence spectra. The output signal of the gated integrator was stored on a computer hard drive using the data acquisition module (SpectraACQ; Horiba Jobin Yvon). As a supplemental spectroscopic system, a gated intensified charge-coupled device (ICCD; DH-720/18U-03 iStar 720D; Andor, Belfast, UK) attached to the spectrometer (SR-303i-A; Andor) was also used to measure the luminescence spectra and lifetimes. In the TRLFS experiment, a long-pass filter of 80% cut-on in the wavelength region of 410–1200 nm (10LWF-400-B; Newport) was inserted in front of the PMT to prevent second-order diffraction signals from scattered laser light and Raman scattering of water onto the PMT at 532 and 594 nm, respectively.

Figure 4 shows the normalized luminescence spectra of a reference solution [5 μg/l U(VI) in a mixed sulfate solution of 0.074 M K$_2$SO$_4$ and 0.074 M H$_2$SO$_4$] and the groundwater sample GW2 pretreated with K$_2$S$_2$O$_8$. These spectra were measured using the ICCD at a gate-delay time of 100 ns and a gate width of 50 μs. The wavelengths of the spectrometer were calibrated using the well-known atomic emission lines of uranium radiated from a uranium hollow-cathode discharge lamp (Palmer et al. 1980). The peak wavelengths (493.1, 514.9, 538.5, and 564.4 nm) in Figure 4 shift up approximately 5 nm compared with those of UO$_2^{2+}$ (488.1, 509.9, 533.0, and 559.4 nm; data not shown). The normalized luminescence spectra for the reference solution and the groundwater sample exhibit...
identical spectral shapes, as shown in Figure 4. Moreover, it should be noted that no significant changes in the spectral characteristics (peak positions and spectral shapes) were found in the kinetic luminescence spectra measured at the different gate-delay times ranging from 0.1 to 25.1 μs with steps of 1 μs (data not shown).

Figure 5 shows the normalized luminescence signal waveforms measured from the same samples shown in Figure 4. The origin of the x-axis indicates the time at which the pulsed laser beam was incident and the laser-induced luminescence was generated. Figure 5 shows the signals integrated from 450 to 625 nm and the identical waveforms for both samples [empty circles for reference solution of 5 μg/l U(VI) and solid circles for groundwater sample GW2]. Figure 5 (solid line) shows the result of fitting the data to the first-order exponential decay function. The average value of luminescence lifetimes measured from reference solutions (uranium concentrations of 5, 10, 20, and 50 μg/l) and groundwater samples (GW1 and GW2) was 11.9 ± 0.4 μs with correlation coefficients better than 0.999. This value is in good agreement with the value of 11.5 ± 0.3 μs for the U(VI)-sulfate complex in the form of UO2(SO4)2− (Geipel et al. 1996).

The results reported in Figures 4 and 5 suggest that the same U(VI) species exist in the reference solutions and the pretreated groundwater samples. Therefore, the uranium concentration in the groundwater samples can be determined using the calibration curve obtained from the reference solutions. Figure 6 shows the calibration curve obtained by plotting the luminescence intensity of the reference solutions at 493.1 nm as a function of the uranium concentration. The circles indicate the mean values obtained from more than six measurements over 3 days (two or three repeated measurement per each day). The error bars correspond to SD. The calibration curve corresponds to a straight line with a correlation coefficient better than 0.999. The uranium concentrations determined in the groundwater samples are shown in Figure 6 (squares) and listed in Table 2 (column 2). The results determined by TRLFS are in good agreement with the results determined using ICPMS, which are listed in Table 1 (column 5).

Because the detection sensitivity of uranium is increased abruptly by the addition of luminescence-enhancing reagents to the sample solutions (Brina and Miller 1992, 1993, Geipel 2006, Kumar et al. 2008), these reagents are always used for the pulsed-laser phosphorimetry, which quantitatively determines uranium using the
Table 2  Total uranium concentrations in the groundwater samples taken from the KURT determined by TRLFS and ratiometric techniques.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Uranium determined by TRLFS (μg/l)</th>
<th>Uranium determined by ratiometric technique (μg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW1</td>
<td>36.2±0.5</td>
<td>36.6±1.4</td>
</tr>
<tr>
<td>GW2</td>
<td>5.3±0.2</td>
<td>5.2±0.5</td>
</tr>
<tr>
<td>GW3</td>
<td>3.5±0.3</td>
<td>3.6±0.7</td>
</tr>
</tbody>
</table>

commercially available KPA instrument. The commercial KPA instrument installed in our laboratory (KPA-11, Chemcheck Instruments, Richland, WA, USA) is equipped with an N₂, laser-pumped dye laser with a center wavelength of 420 nm, PMT detectors, and multichannel scalers to count the photons generated from the time-resolved laser-induced luminescence. The luminescence-enhancing reagent, called Urplex, used in this commercial instrument can increase the luminescence lifetime of uranium up to several hundred microseconds; as a result, the luminescence of uranium is categorized as phosphorescence. After irradiation by each laser pulse, the decay of the phosphorescence signal waveform is further analyzed based on the principle that the y-intercept value obtained by extrapolating a plot of the measured phosphorescence intensity as a function of time is proportional to the concentration of uranium (KPA-2009). This y-intercept value corresponds to a theoretical phosphorescence intensity, which is dependent only on the U(VI) concentration and not on dynamic quenching effect due to the presence of quenchers in the sample. Along with sample pretreatment procedures, including the addition of Urplex, pulsed-laser phosphorimetry provides an LOD of approximately 0.01 μg/l.

In the present work, it is noteworthy that the luminescence lifetime of the U(VI)-sulfate complex in the reference solution increased from 11.9±0.4 to approximately 275 μs (data not shown) when the luminescence-enhancing reagent (Na₄P₂O₇+H₃PO₄) used in a previous study (Cho et al. 2013) was added to the reference solution. This effect may improve the LOD by approximately 15-fold due to the enhanced luminescence intensity.

Ratiometric technique using the ratio of U(VI) luminescence to the Raman scattering of water

In the TRLFS, a calibration procedure must be performed for each day of operation to eliminate analytical errors generated by the variations in the laser pulse energy and the drifts of the high voltage supplied to the PMT. Thus, repeating the procedure used to prepare the calibration curves can be time consuming. To improve this cumbersome procedure, a simple ratiometric technique based on the simultaneous measurement of U(VI) luminescence and the Raman scattering of water was developed to determine the concentration of U(VI) in aqueous solutions (Cho et al. 2013, Jung and Cho 2014). In this technique, the calibration curve can be obtained by measuring the ratio of the U(VI) luminescence intensity to the Raman scattering intensity of water. When the Raman scattering intensity of water acts as an internal standard signal for the quantitative analysis of U(VI), the calibration curve can be used continuously because the slope of the calibration curve remains unchanged despite fluctuations in the power of light source and the sensitivity of the detector (see Figure 4B in Cho et al. 2013).

One advantage of this ratiometric technique is that both pulsed and CW lasers can be used. In a previous work, a CW semiconductor laser beam at a center wavelength of 405 nm was used as the light source (Cho et al. 2013). For comparison, a pulsed Nd:YAG laser (Minilite; Continuum) beam at 266 nm was used as the excitation light source in the present experiment. Figure 7 shows representative spectra for deionized water purified by a Milli-Q system (Elements; Millipore Co.), reference solutions (uranium concentrations of 2 and 10 μg/l), and groundwater sample GW2. These spectra were measured using the same experimental system described in Figure 3, with a gate-delay time of 100 ns and a gate width of 15 μs. In the present

![Figure 7](image-url)
ratiometric experiment, the long-pass filter used in the TRLFS experiment was removed to measure the Raman scattering intensity of water because the Raman peak of water corresponding to a wavenumber shift of 3375±42 cm⁻¹ (Walrafen 1964) appears at 297 nm with an excitation wavelength of 266 nm. The distinctive luminescence peaks of U(VI) appear at 493.1 and 514.9 nm, as shown in Figure 7. The peaks from the second-order diffraction of the excitation wavelength and the Raman peak appear at 532 and 594 nm, respectively. It is apparent that the luminescence intensities of uranium depend only on the uranium concentrations, whereas the Raman intensities of water at 297 nm remain almost unchanged for all samples.

Figure 8 shows the calibration curve obtained by plotting the ratios of the U(VI) luminescence intensity at 493.1 nm for reference solutions to the Raman intensity of water at 297 nm as a function of the uranium concentration. The circles indicate the mean values obtained from three different measurements, and each measurement was performed at PMT voltages of 750, 800, and 850 V. The error bars correspond to SD. The calibration curve is a straight line with a correlation coefficient better than 0.998. This result confirms that the ratio of the U(VI) luminescence intensity to the Raman intensity of water is not affected by variations in the laser pulse energy and the drifts of the high voltage supplied to the PMT. The determined uranium concentrations in the groundwater samples are shown in Figure 8 (squares) and listed in Table 2 (column 3). The results determined using the ratio of U(VI) luminescence intensity to the Raman intensity of water are also in good agreement with the results obtained by ICPMS and TRLFS listed in Tables 1 and 2, respectively.

Figure 8 (inset) represents the luminescence spectrum for the reference solution, with uranium concentration of 0.2 µg/l. A comparison of the luminescence intensity at 493.1 nm for the reference sample with 3σ, where σ is the SD of the background intensity at 493.1 nm for the blank solution without uranium, resulted in an LOD of approximately 0.03 µg/l. This value is sufficiently sensitive for monitoring the trace amount of uranium in drinking water and ensuring that it is low enough to prevent ingestion (MCL of 30 µg/l). Based on these results, we propose a very simple analytical system for determining the uranium concentration in water, as shown in Figure 9. In the proposed system, the LOD can be improved using the appropriate optical filters, so that the PMT will only detect the luminescence at the peak wavelengths of the analytes and achieve the best signal-to-noise ratio. The filters replace the monochromator.

**Summary**

The present work reviewed the analytical techniques used for the determination of uranium in aqueous solutions. Laser-based spectroscopic techniques, TRLFS, and recently developed ratiometric techniques based on the
measurement of laser-induced luminescence of U(VI) were reviewed in detail. The advantage of these techniques in comparison with the well-known ICPMS and radiochemical spectrometry techniques is that high precision with low LOD can be achieved using relatively simple experimental apparatuses and procedures. The performance of these techniques was verified by determining the uranium concentrations in the groundwater samples taken from the KURT. The NOM in groundwater, which may interrupt the quantitative analysis of uranium due to the spectral overlap in the luminescence between NOM and uranium, was removed using the wet oxidation method with K$_2$S$_2$O$_8$. The results determined using TRLFS and ratiometric techniques are in good agreement with the results determined by ICPMS. An LOD of 0.03 μg/l was achieved using these laser spectroscopic techniques.

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