

Uranium Fluorescence Analysis in the Raffinate Solution of Nuclear Fuel Conversion Process Using Time-resolved Laser-induced Fluorimetry

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레이저 유발형광법을 이용한 변환공정 폐액중의 우라늄 형광분석

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Abstract

A simple and new uranium analysis technique for raffinate solution of nuclear fuel conversion process was developed using a time-resolved laser-induced fluorimetry. The addition of 4 M-phosphoric acid more than 10 times in volume to the raffinate sample was found to be efficient for obtaining stable uranium fluorescence signal which was not influenced by many fluorescence quenchers. A calibration curve of a good linearity for the fluorescence intensity vs. the uranium concentration was obtained at the range of 3.0×10^{-6} – 6.0×10^{-5} M UO_2^{2+} in the raffinate samples.

요 약

원자력 산업의 변환공정에서 발생하는 폐수용액중의 우라늄 농도를 레이저 유발형광법을 사용하여 쉽게 측정할 수 있는 새로운 분석방법을 개발하였다. 실험 결과 시료의 약 10배 이상의 부피로 4M-인산용액을 첨가함으로써 효율적으로 형광 quencher의 영향을 배제시킬 수 있었으며, 폐액 시료에서의 우라늄 농도 3.0×10^{-6} – 6.0×10^{-5} M UO_2^{2+} 의 범위에서 농도에 대한 형광강도의 직선성이 우수하였다.

1. Introduction

The uranium concentration in raffinate solution of nuclear conversion process is estimated to be ca. 4.2×10^{-5} M (10 ppm). The quantitative analysis of uranium is necessary to improve uranium economy or to protect the environment from water pollution. However, the analysis of uranium in raffinate solution is difficult due to its complicated

components(NO_3^- , Fe^{2+} , Ca^{2+} , Mn^{2+} , etc.) and high acidity($pH < 1$). The conventional methods, such as the chromatography, the α -particle counting techniques, the neutron activation, the mass spectrometry, and so on, have been utilized to the analysis of raffinate solution [1–3]. These methods are inconvenient and time-consuming due to the complicated sample treatment or the large instrumentations. The main compositions of

Table 1. The Chemical Components of the Raffinate Solution in Nuclear Conversion Process.

Comp.	Conc.(ppm)	Comp.	Conc.(ppm)	Comp.	Conc.(ppm)
Fe	1600	Al	363	Si	21
Cu	2.7	Pb	2.4	Mo	4.6
Cr	2.3	Ca	76	NO ₃	37000
Mg	64	Sn	0.6	Co	0.7
Ni	0.9	B	2.0	Zn	4.4
Mn	61	U	12		

Acidity : pH 0.14

the raffinate solution are listed in Table 1 [4].

The laser-induced fluorimetry is considered to be a powerful and simple method for the quantitative analysis of uranium. However, for the application to the sample with complex matrix like the raffinate solution, the laser-induced fluorimetry has some limitation due to the fluorescence quenching by Fe, Mg, Ca or NO₃⁻, etc.

In case of the time-resolved laser-induced fluorimetry, it is easy to reduce the procedures of sample treatment by the simultaneous use of wavelength resolution and time resolution of fluorescence. For the purpose of finding out a simple analytical method for the raffinate solution, we utilized the characteristics of the time-resolved laser-induced fluorimetry. Since the phosphoric acid was known to make a stable complex with uranyl ion[5], the additive effects of phosphoric acid were investigated.

2. Experimental Sections

A home-made N₂-laser induced fluorimeter was used in this experiment, and the details are described elsewhere [6-9]. The excitation source was a N₂ laser (Laser Science Inc.), peak power 40 kW, repetition rate 10 pps, and output energy 120 μ J/pulse. The fluorescence lifetime and the intensity of fluorescence at time zero were measured by using a 4-channel A/D converter with

resolution of 8 bits, which was connected to a personal computer (compatible with IBM 286 AT) through a RS-232C interface. The time evolution of uranium fluorescence intensity induced by a pulsed N₂ laser revealed an exponentially decaying curve. Using the integrated values of the two gates on the fluorescence decaying curve, the fluorescence lifetime and the fluorescence intensity at time zero were calculated [8]. The delay time or the gate time control in the fluorimeter can be done by a step of 1 μ s.

3. Results and Discussion

Phosphoric acid is known to improve photo-emission intensity of the uranyl ions at wavelengths of 501, 521, 543, and 570 nm by making a complex with uranyl ions [10]. In this experiment, we investigated the additive effects of phosphoric acid to the raffinate samples of nuclear fuel conversion process. The standard solutions of uranium were prepared by dissolving UO₂ powder in the concentrated nitric acid and diluting with distilled water.

The uranium fluorescence intensity as a function of the phosphoric acid concentration is displayed in Fig. 1. The samples were prepared by adding 0.5-10 M phosphoric acid to the raffinate solution. The volume percentage of raffinate in the

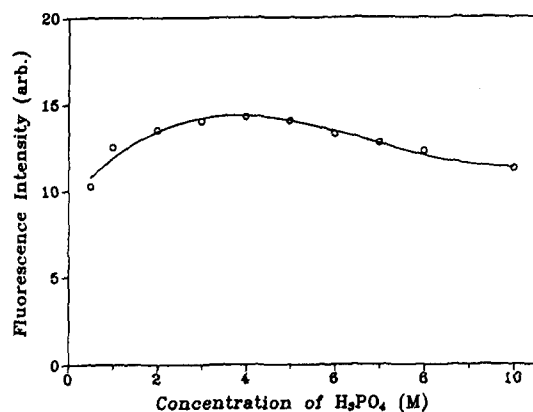


Fig. 1. The Intensity of Uranium Fluorescence as a Function of the Phosphoric Acid Concentrations in the Raffinate Samples ($[\text{Raffinate Solution}] / ([\text{Phosphoric Acid}] + [\text{Raffinate Sample}]); 3\%$)

sample solution was ca. 3%. The results showed that the addition of 3–5 M phosphoric acid was good enough to obtain a high intensity of uranium fluorescence.

In case of the measurement of fluorescence intensity, the dilution effect on collisional quenching caused by the addition of additives reveals to be exponential, though the effect on fluorescence signal intensity is linear. Therefore the maximum dilution is necessary to the sample including large amount of fluorescence quenchers like a raffinate solution at the sacrifice of the signal intensity decrease. Table 2 shows the additive effects of 4 M-phosphoric acid to the raffinate solution. The fluorescence intensity and the fluorescence lifetime were measured as a function of the raffinate percentages in the sample solutions diluted by 4 M-phosphoric acid. The fluorescence intensities were varied with the raffinate percentages. It was shown that the raffinate contents less than 10% were necessary in order to obtain stable fluorescence lifetimes regardless of the addition of phosphoric acid. At higher raffinate percentages, the fluores-

Table 2. Uranium Fluorescence Characteristics of the Raffinate Samples as a Function of the Raffinate Percentages in 4M-Phosphoric Acid.

Raffinate Percentage(%)	Fluorescence Lifetime(sec)	Fluorescence Intensity(arb.)
1	9.5×10^{-5}	5.3×10^{-6}
2	1.1×10^{-4}	8.3×10^{-6}
5	1.2×10^{-4}	1.6×10^{-7}
9	1.2×10^{-4}	3.0×10^{-7}
17	8.6×10^{-5}	4.4×10^{-7}
33	5.1×10^{-5}	7.8×10^{-7}
50	3.3×10^{-5}	1.1×10^{-8}
60	2.9×10^{-5}	1.2×10^{-8}

ence lifetime was shown to be decreased. It is due to the increase of quenching effect by various ions in the raffinate solution.

Fig. 2 demonstrates the time evolution of the fluorescence intensity emitted from a raffinate–4 M phosphoric acid mixture which was measured by a oscilloscope, LeCroy 9400A. Though the fluorescence for raffinate sample was unmeasurable, the addition of phosphoric acid made the fluorescence measurement possible. Fig. 2 shows that fluorescence intensity decreases with the decrease of the raffinate percentages. However, fluorescence lifetime shows the opposite trend. The high fluorescence intensity at a high raffinate percentage is considered to be resulted from the net increase of uranium content. But the decrease of fluorescence lifetime at a high raffinate content is thought to be due to the increasing quenching effect. Therefore, in an appropriate range of raffinate content, the phosphate ions would make a stable uranyl complex in the acidic uranium aqueous solution ($\text{pH} < 3$).

The calibration curve of the fluorescence intensity vs. the uranium concentration is displayed in Fig. 3. The calibration data were obtained using a raffinate solution added by standard uranium and 4 M-phosphoric acid solution. The uranium

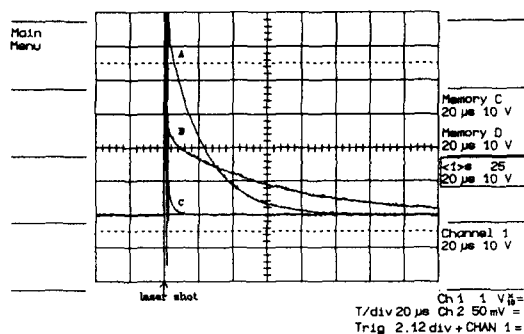


Fig. 2. Time Evolution of Uranium Fluorescence Intensity of the Raffinate Solutions at a Various Raffinate Percentages in the Phosphoric Acid Solution(A ; 60%, B ; 20%, C ; 100%).

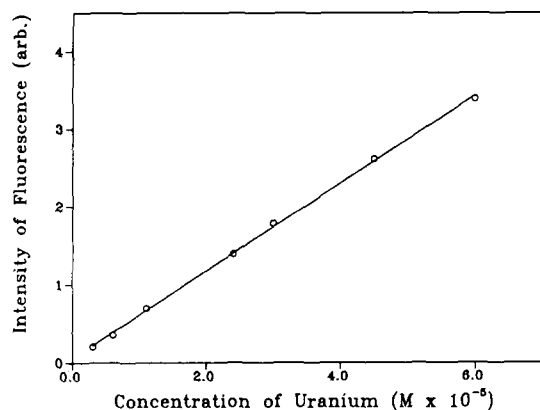


Fig. 3. The Calibration Curve of Uranium Fluorescence Intensity in a Raffinate Samples Mixed with 4 M-Phosphoric Acid. The Different Uranium Concentration of Each Solution Was Made by the Addition of Standard Uranium Solutions. ([Raffinate Sample] / ([Phosphoric Acid] + [Raffinate Sample])); 5%

concentrations of the measurement samples were controlled to be within the range of 3.0×10^{-6} – 6.0×10^{-5} M UO_2^{2+} . And the raffinate contents in the measurement samples were made to be 5% by adding 4 M-phosphoric acid. The

calibration data revealed that the addition of phosphoric acid to the raffinate sample was very efficient to the quantitative analysis of uranium.

4. Conclusions

A simple method for the quantitative uranium analysis in the raffinate sample was developed using a time-resolved laser-induced fluorimetry. The addition of phosphoric acid was efficient to prevent the quenching effects from the various quenchers included in the very acidic raffinate samples (pH 0.14). A good calibration curve of fluorescence intensity vs. uranium concentration was obtained at the range of 3.0×10^{-6} – 6.0×10^{-5} M UO_2^{2+} by adding 4 M-phosphoric acid to the raffinate samples.

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