

An Improved Laser-Induced Fluorimetry for Assay of Uranium in Urine

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레이저 유발형광법을 이용한 우라늄 작업자의 뇨 형광 분석

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Abstract

A method for analysis of trace uranium in urine sample was studied using a time-resolved N_2 -laser-induced fluorimetry. The Fluran solution was found to be efficient to mask the chloride ions which are known to quench uranium fluorescence in the fluorimetric assay of uranium in urine. This improved method made the sample preparation much simpler than other conventional ones. The fluorescence intensities at 1% urine mixture with 10% Fluran aqueous solution showed good linearities in the concentration range of 10–500 ppb (before dilution).

요 약

펄스형 질소레이저를 사용한 time-resolved laser-induced fluorimetry를 이용하여 우라늄 작업자의 뇨속에 함유되어 있는 우라늄의 농도를 간단한 전처리만으로 정량분석하는 방법을 연구하였다. 형광분석할 때에 뇨에 함유된 chloride ion은 우라늄 형광을 심하게 quenching 하는 것으로 알려져 있으며, 따라서 이를 제거하기 위한 전처리 과정에서 많은 시간 소모와 큰 실험 오차를 유발하고 있다. 본 방법에서는 10% Fluran 수용액을 뇨에 첨가하여 뇨함량이 약 1% 정도가 되었을 때 뇨속의 chloride에 의한 quenching 영향을 최소한으로 줄일 수 있었으며, 시간 0에서의 형광강도를 계산하여 형광강도의 농도에 대한 직선성을 측정된 결과 우라늄 농도 범위 10–500 ppb에서 우수한 직선성을 나타내었다.

1. Introduction

The deposition of uranium in human bodies occurs in the course of handling uranium in conversion or fuel fabrication process. The inhalation of yellow cake, U_3O_8 , or ammonium diuranate,

$[(NH_4)_2U_2O_7]$, is hazardous due to their radiotoxicity particularly to the kidneys. The International Atomic Energy Agency (IAEA) recommends to keep the uranium concentration below 1.8×10^{-7} Mol/liter ($60 \mu\text{g}$ per 1.4 liter-urine which is the estimation of total urine amount delivered per

day)[1]. The solubility of ammonium diuranate in blood is larger than that of U_3O_8 [2~4]. The uranium exists in the form of uranyl ion, UO_2^{2+} , in the body fluid and is delivered with urine.

The conventional analyses of uranium in urine samples were performed by chromatography, α -particle counting techniques, neutron activation, and mass spectrometry[5~7]. These methods are generally time-consuming and expensive, and result large errors due to their complex procedures for sample preparation.

Time-resolved laser-induced fluorimetry is one of the powerful methods for the trace analysis of fluorescent materials due to the excellent monochromaticity and the high peak power of the laser. In addition, the method makes the sample preparation much simpler because it uses the characteristics of wavelength resolution and time resolution of the fluorescence, simultaneously. Since the fluorescence intensity at time-zero, which can be calculated using a computer, is not influenced by quenchers, the method is useful for application to samples in which many quenchers are dissolved.

In this paper, we report a new and useful method for trace uranium analysis in urine samples using time-resolved laser-induced fluorimetry.

2. Experimental Section

The experiment was performed using a laser-induced fluorimeter built at KAERI. The schematic diagram of the experimental set-up is given in Fig. 1. The details of the instrument are described elsewhere[8~10]. In a preliminary experiment, the bias voltage of the photomultiplier(PM) tube was set to be -910 V in order to improve detector sensitivity to the fluorescence intensity which was very weak in trace analysis. The fluorescence near 450 nm from organic molecules was blocked out using an optical interference filter. The transparent

wavelength range of the filter was 470~540 nm.

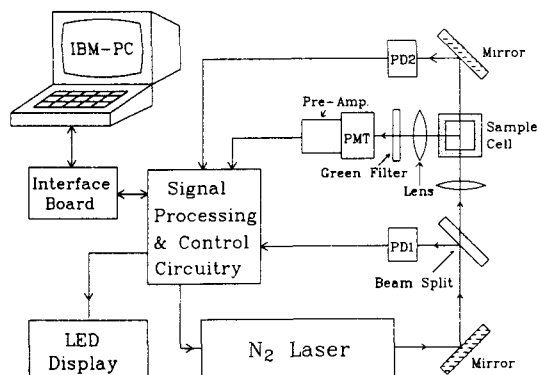


Fig. 1. Schematic Diagram of the Experimental Set-Up

The fluorescence signal from a PM tube was measured using a digital storage oscilloscope (LeCroy 9400A, BW 175MHz). The delay time and the gate time were optimized by taking into consideration of the lifetime of fluorescence signal. The fluorescence intensity at time zero was calculated using the integrated values from two gates on the fluorescence time-evolution curve[9] which decays exponentially. It was possible to reduce experimental error by using the fluorescence intensity at time-zero which is unaffected by various quenchers. The two-interval integrations were conducted 30 times and averaged to reduce the effects of random electrical noise.

Urine samples were treated with concentrated sulfuric acid and filtered. The standard solutions were prepared by adding known concentrations of uranium aqueous solution which was made by dissolving UO_2 powder in 10 Mol/liter nitric acid. Fluran (Scintrex, Canada) aqueous solutions (5%, 10%, 50% and 100%) were added to each urine sample.

The fluorescence lifetime of uranyl ion was found out to be about 50 μ s. The delay time was chosen to be in the range of 8~16 μ s, depending on the oscilloscope gain, and the gate time

was controlled to be 12 μ s.

3. Results and Discussion

Phosphoric acid is one of the good additives for trace uranium fluorescence analysis for enhancing uranium fluorescence intensity. However, in the case of uranium samples including significant levels of plutonium or various kinds of fluorescence quenchers, the addition of sulfuric acid[10] or Fluran[11] was recommended, respectively. Especially, the urine samples in which chloride ions are present in large concentrations are difficult to be analyzed using uranium fluorescence analysis due to the serious quenching by the chloride ions (quenching coefficient, $k_q > 10^8 \text{ M}^{-1} \text{ S}^{-1}$)[12]. In this experiment, the additive effects of phosphoric acid and Fluran were studied in order to choose an appropriate additive for the trace uranium analysis in urine samples.

Fig. 2 shows the effect of chloride on the fluorescence intensity in the case of adding phosphoric acid or Fluran to the 500 ppb uranium aqueous solution in which 0.5% of NaCl was dissolved. As shown in Fig. 2, the experiment

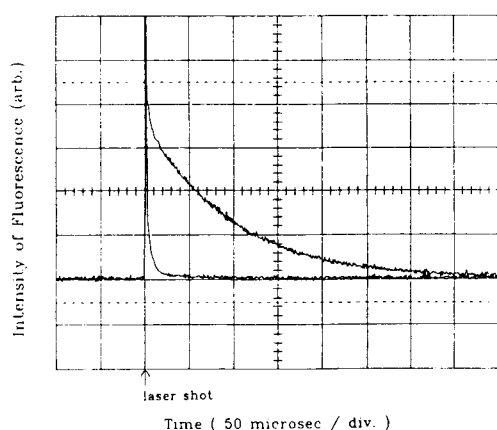


Fig. 2. The Effects of Chloride Ion on the Fluorescence Signal Intensities. (Upper Curve: Fluran Solution Added, Lower Curve: 4M Phosphoric Acid Added)

revealed that the addition of phosphoric acid was not enough to eliminate quenching by the chloride ions. However, the addition of Fluran resulted in high intensity uranium fluorescence, which would be due to the stable complex formation between Fluran and the uranyl ions. The Fluran molecule would protect the uranyl ion from attacks of chloride by shielding the excited uranyl ion[11]. The dependence of fluorescence intensity on the concentration of Fluran was investigated by measuring the dilution effects of Fluran. Table 1 shows the fluorescence intensity variations of urine samples including 500 ppb of uranium. The Fluran solutions of each concentration were added to the urine samples. The Fluran addition ratio was chosen to be 100 in consideration of the expected uranium concentration levels of $\mu\text{g/liter}$ in urine and the optimum detection range of the instrument (0.05–100 ppb). The addition of 10% Fluran solution was found to be enough to obtain a relatively high and stable fluorescence signal intensity.

Table 1. The Fluorescence Intensities of Urine Samples Including 500 ppb Uranium vs. Fluran Concentrations.

Fluran Conc.(%)	5	10	50	100
Fluorescence Intensity(arb.)	83	95	96	98

Table 2. The Uranium Fluorescence Intensities of Urine Samples Diluted by 10% Fluran Solution.

Urine Conc.(%)	4	2	1.25	1	0.8	0.6
Fluorescence Intensity(arb.)	76	80	87	85	81	77

Table 2 shows the effects of dilution using 10% Fluran solution. For successful removal of the chloride quenching, the most convenient method is to dilute the sample. The maximum dilution is necessary to keep the chloride concentration as

low as possible at the sacrifice of fluorescence intensity. The dilution effect on the quenching is known to be exponential, but that on the signal intensity is linear. It was found that the urine concentration of 1–1.25% (dilution of ca. 80–100 times) was optimum for obtaining a high fluorescence intensity.

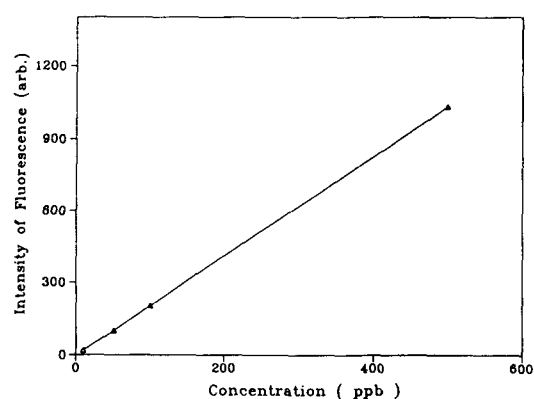


Fig. 3. The Calibration Curve of Fluorescence Intensity vs. Uranium Concentration in Urine Samples.

The calibration curve of fluorescence intensity vs. uranium concentration was obtained. The sample was prepared by adding 100 times of 10% Fluran solution to the urine sample, to which the standard uranium solution was already added. Fig. 3 reveals that the calibration curve is good enough to be used in the quantitative analysis of trace uranium in the urine sample in the concentration range of 10–500 ppb (before dilution).

4. Conclusions

A simple method for trace uranium analysis of urine sample was developed using a

time-resolved N_2 -laser-induced fluorimetry. The urine sample could be easily prepared only after treating the urine with sulfuric acid and filtering the organic solids. The addition of 80–100 times of 10% Fluran solution to the urine sample was enough to eliminate fluorescence quenching by chloride ions. This method could be applied to monitoring of uranium in human bodies by checking the uranium concentration in urine samples.

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