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An Apparatus for Monitoring Real-time Uranium Concentration Using Fluorescence Intensity at Time Zero

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Abstract

An apparatus for detecting remote real-time uranium concentration using an optrode was developed. An optrode to detect uranium fluorescence as remote real-time control was designed. Fluorescence intensity at time zero was derived by the fluorescence signal processing and the algorithm to exclude the quenching effect of various quenchers and temperature fluctuations. This apparatus employing the above deriving method and the optrode has an error range within 6% in spite of serious fluorescence lifetime changes due to the quenching effect and temperature fluctuations. The detection limit is 0.06 ppm and the linearity is excellent between 0.06 ppm and 2 ppm on the aqueous uranium solution.

Key Words : uranium, real-time fluorimeter, quenching effect, quencher

1. Introduction

The analysis of remote real-time uranium concentration under a highly radioactive environment has been extensively studied. Also, the real-time monitoring of uranium concentration to minimize the loss of end product on the ion exchange extraction process has been considerably studied. In the past, the measurement of remote real-time uranium concentration[1-3] was implemented by the optrodes based on the fluorimetric technique. It had the disadvantages of the high detection limit, the preparation process and the complicated structure. In addition, there was no proper method to compensate for the effect of quenchers and temperature fluctuations. In recent years, these disadvantages could be overcome in many parts due to the progress of remote control technologies, optical fibers and pulsed-lasers.

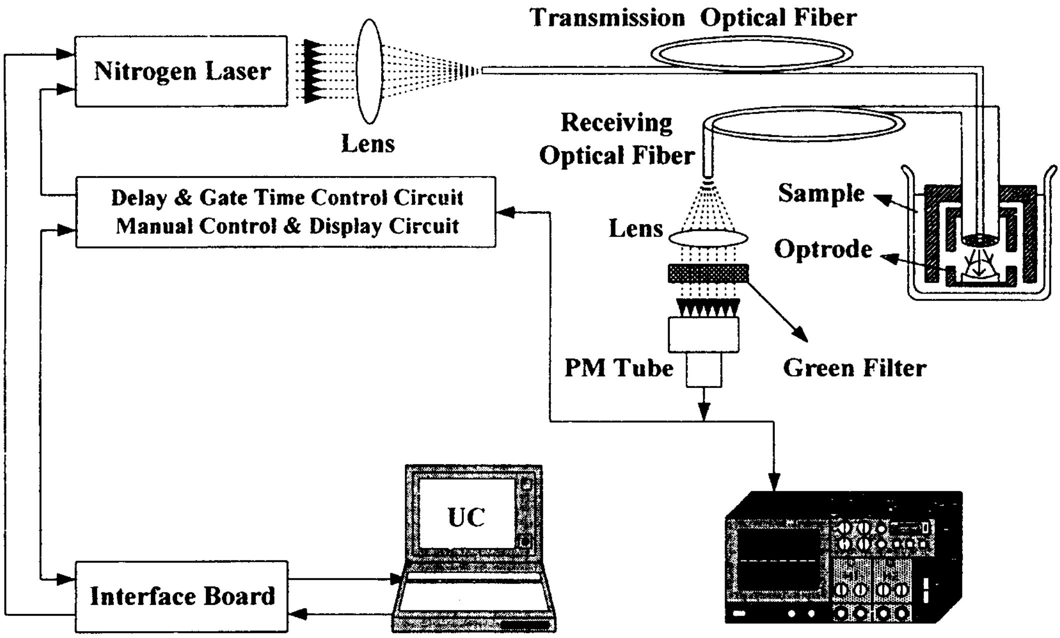

Fig. 1. Experimental Apparatus

This paper studies the laser-induced time-resolved fluorimetric technique[4-10] which performs the function of continuous remote real-time monitoring without using the fluorescence enhancing buffer solution. To exclude the effect of fluorescence lifetime quenchers and temperature fluctuations, a derivation method of the fluorescence intensity[6] at time zero is applied. It can provide more precise analysis without the preparation of samples. In this study, the optrode is very simply structured with a concave mirror and several optical fibers. A concave mirror is used to reflect and collect the laser beam and the uranium fluorescence. It allows the detection limit to be lowered than before. For this study, two sensing structures are designed and tested: One is for the various samples to be exposed to the external light and the other is for the various samples to be shielded from the external light. The elimination of the noise generated by external light to improve the detection limit of uranium concentration should be considered.

2. Experimental

2.1. Apparatus

Fig. 1 shows the scheme for a remote real-time uranium fluorimeter to monitor uranium concentration. It consists of the optrode, the long optical fibers, the software for system operation, the IBM-PC and the N_2 laser as excitation source. An IBM-PC and an interface board with the functions of A/D(Analog to Digital) conversion and DO(Digital Output) are employed for processing the algorithm to derive the fluorescence intensity at time zero.

The optrode is used to detect uranium fluorescence generated by the transmitted laser beam and it is composed of a concave mirror and several optical fibers. The length of the optical fiber for the transmission of laser beam is about 6-

meters and the optical fiber for receiving uranium fluorescence generated by laser beam is about 4-meters. The optical fibers (Fiber Guide Ind, center : ϕ =1mm, external : ϕ =0.7mm) have no transmission loss at 337 nm wavelength of excitation source and around 540 nm wavelength of uranium fluorescence.

The designed software for monitoring real-time uranium concentration includes the functions of laser trigger pulse generation, data acquisition, the data processing and display function for displaying the analyzed uranium concentration. The IBM-PC is used for real-time process signals obtained from interface board. The interface board is used to convert the analog signals to the digital signals (A/D converter) and to generate a laser trigger pulses through the digital output port for triggering N_2 laser. The A/D converter has a high resolution of 12 bits and relatively high speed of 10^6 samples/sec.

The analog system of the fluorimeter consists of four parts: analog integrators, gate and delay intervals generation part, PM(Photo-Multiplier) tube and pre-amplifier. The pulsed-nitrogen laser (Laser Science Inc.) with the 40 kW peak power, 3 ns pulse width, 200 μJ average power, $\pm$3% power stability at 10Hz, 1 to 20 pps pulse intervals is used as excitation source with the external trigger function. The green filter(Melles Griot) with the transmission wavelength between 490 nm and 580 nm is used to exclude the noise generated from external light sources with various wavelengths.

The delay and the gate intervals are controlled to derive the fluorescence value at time zero on the exponential decay curve depends on time. Two quartz lens(45 mm and 75 mm of focal length) are used to collect the laser beam and uranium fluorescence to reduce transmission loss. The oscilloscope(LeCroy 9400 digital storage, bandwidth = 125 MHz) can capture the fluorescence signal amplified by a pre-amplifier is employed to observe the rationality and the lifetime of signal.

2.2. Optrode for Sensing Fluorescence

The Fig. 2 shows the structure of optrode to detect the remote real-time uranium concentration. According to the samples to be detected, two types of optrodes are designed: i) The optrode named ELO(External Light Optrode) is designed for the samples to be exposed to the external light and it is shown in Fig. 2(a). ii) The optrode named DEO(Dark Environment Optrode) is designed for the samples in the dark environment and it is shown in Fig. 2(b). Each of ELO and DEO is composed of a concave mirror, two optical fibers, and Duralumin structures.

ELO consists of three parts: the internal, external and rear parts. Both the center of ELO and the center of the transmission optical fiber have the same axis to collect laser beam and uranium fluorescence generated by laser beam. The internal and the external parts have the same axis and they are fastened in order to fix the optical fibers for the transmission of laser beam and uranium fluorescence. The internal part has four large holes to help the free flow of sample solution and the long screw has a small holes to fix several optical fibers. Also, there is a 2 mm gap between the internal part and the external part for the free flow of sample solution. The external part is shielded from the external light source. The rear part is shown in Fig. 2(c) which is designed with a concave mirror to collect the reflected light of the laser beam and uranium fluorescence. A concave mirror with f=12 mm focuses the laser beam and collects the uranium fluorescence generated by the focused laser beam. It is fixed to the internal part through a screw. The screw can control the point to focus the light reflected by the concave mirror.

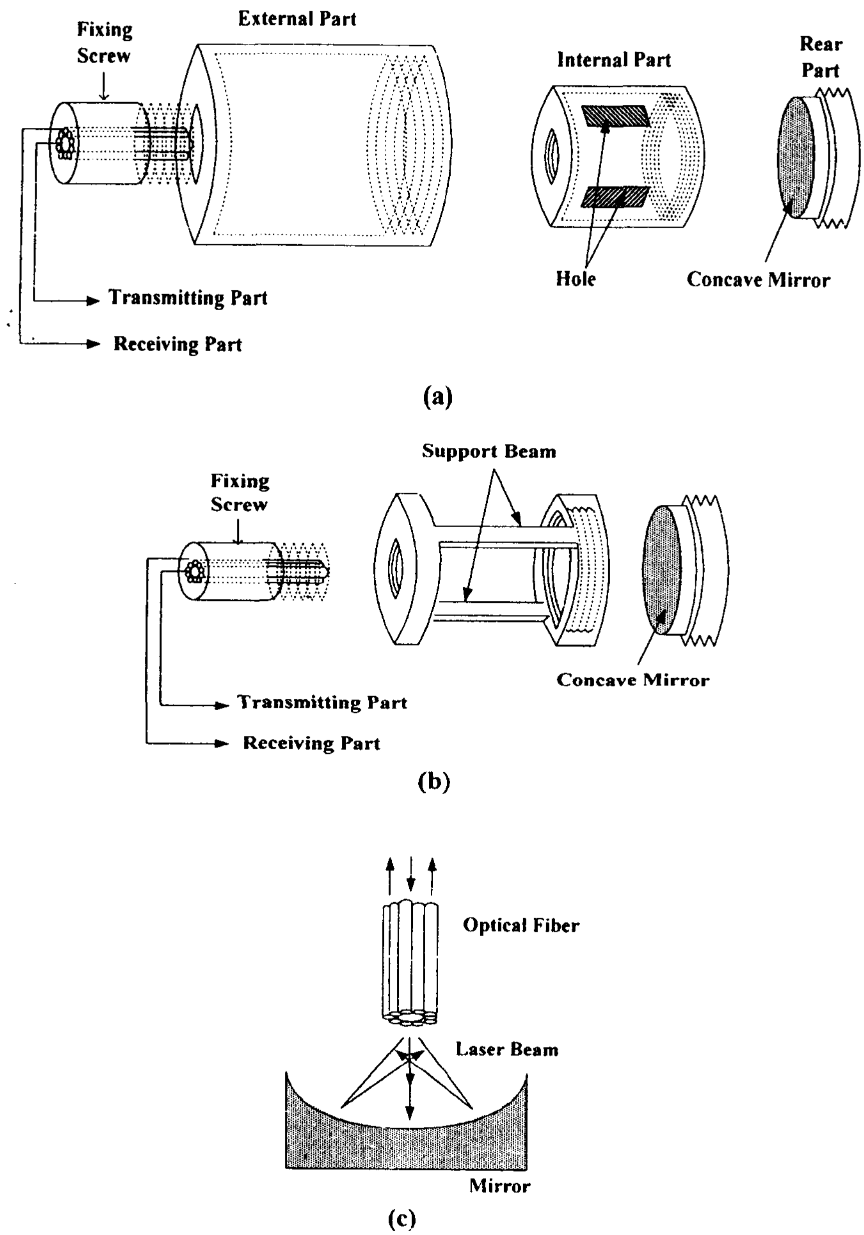

Fig. 2. The Structure of Optrodes
(a) ELO, (b) DEO, (c) Light reflection at the ELO and the DEO

A concave mirror could be increased the uranium fluorescence generated by laser beam and thus the detection limit could be lowered.

DEO(size; height 35 mm, ϕ =24mm) can be designed as the very simple structure which is supported by two beams instead of external and internal parts. It can freely flow to the various samples solution and it easily adapts to against the concentration change of samples. A concave mirror used for ELO is also used at DEO.

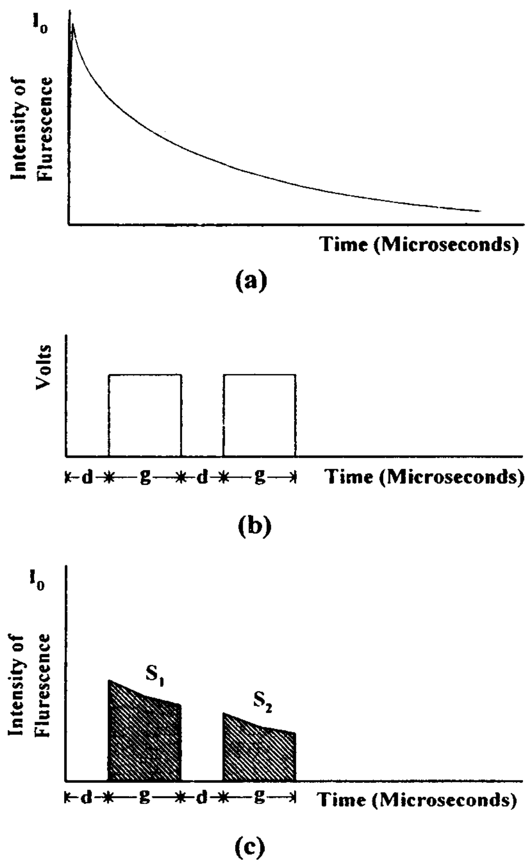

Fig. 3. The Derivation Method of Fluorescence Intensity at Time Zero
d ; delay interval, g ; gate interval, S_1 ; integrated value during g interval(front), S_2 ; integrated value during g interval(rear), I_o ; fluorescence intensity at time zero, : fluorescence lifetime

2.3. Signal Processing

Fig. 3(a) shows the method to derive the fluorescence intensity at time zero. Fig. 3(b) shows the pulse width for determining the intervals of gate and delay using the ON/OFF of the CMOS analog switches. S_1 and S_2 (Fig. 3(C)) are the values integrated during the gate intervals and they are used to derive the fluorescence intensity at time zero. The equation[6] for deriving the fluorescence intensity at time zero without the effect of quenchers and the temperature fluctuation is given by

$$I_o = S_1/(\tau e^{-d/\tau}(1-e^{-g/\tau})) \quad (1)$$
$$= (1/(d+g)) \times S_1 \ln(S_1/S_2)(S_1/S_2)^{d/(d+g)} \times (1-(S_1/S_2)^{-g/(d+g)})^{-1}$$

Where, I_o is the fluorescence intensity at time zero and τ is the fluorescence lifetime[6] which is given by

$$\tau = (d + g) / \ln(S_1 / S_2) \quad (2)$$

In the Fig. 5, the lifetime of uranium fluorescence on the standard solution is about 34 microseconds. The gate and delay intervals[6] are fixed to 7μs and 10μs considering S/N(Signal to Noise) ratio[6] and fluorescence lifetime. The delay or gate intervals in this fluorimeter can be controlled as a step of 1μs unit. The integrator consists of a low leakage MF(Metalized Film) capacitor and two CMOS analog switches with a FET element in an input port. The input impedance of the two CMOS analog switches to control the gate interval and reset signal has 1 GΩ when they are turned off. Two integrated values(S_1, S_2) are held at a capacitor during 3 ms for A/D conversion.

Fig. 4 shows the signal flowchart to operate a remote real-time uranium fluorimeter with the function to compensate for the effect of lifetime quenchers and temperature fluctuations. It takes about 10 seconds from the starting time generated by the trigger pulse to time for displaying uranium concentration on the monitor. The designed software for operating this apparatus was used to control the time interval for a cycle from several seconds to unlimited time. For more precise analysis, integrated values are added 20 times and averaged.

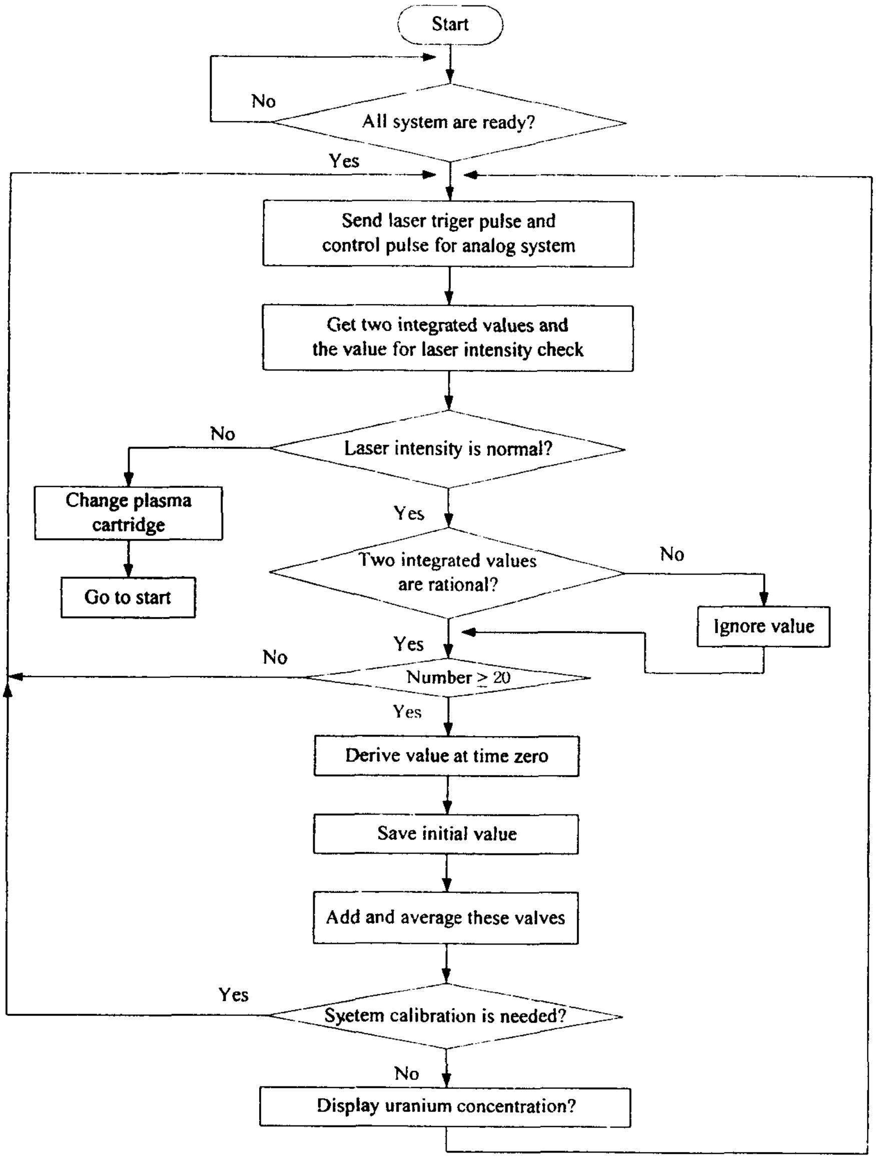

Fig. 4. Signal Processing for Continuous Remote Real-time Uranium Concentration Monitoring

3. Results and Discussions

3.1. Effect of Quenchers

The method to derive fluorescence intensity at time zero using the values integrated during two gate intervals is implemented to a fluorimeter for detecting the remote real-time uranium concentration without sample preparation on aqueous solution. Fig. 5 shows fluorescence signals from the sample solution which adds quenchers[8-10](0.02 M Mn^{2+} or 0.04 M Ca^{2+}) on aqueous uranium solution of uranium (1 ppm UO_2^{2+}, pH=6). Each of the fluorescence intensity

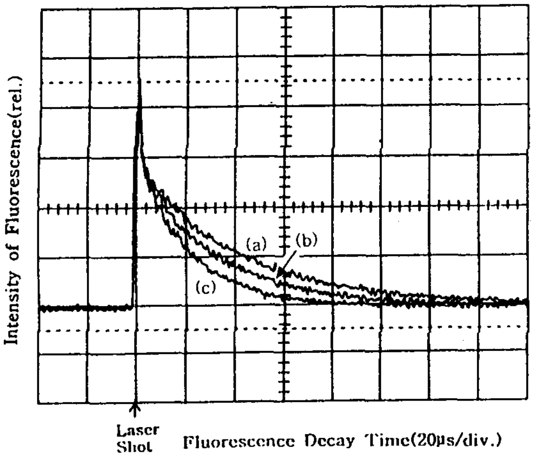

Fig. 5. Fluorescence Signals on Uranium *Aqueous Solution with or Without* Lifetime Quenchers. (upper(a); neat UO_2^{2+} Solution, Middle(b); Ca^{2+} Added, Lower(c); Mn^{2+} Added)

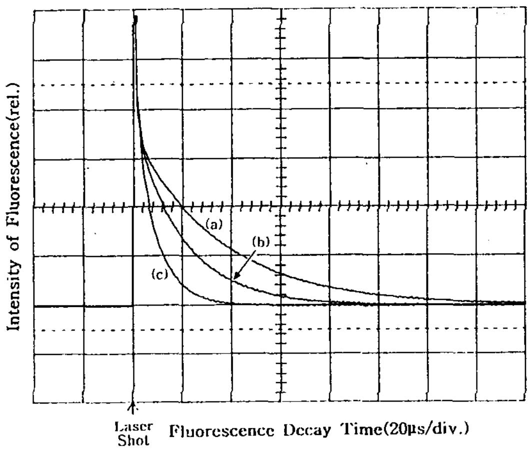

Fig. 6. Fluorescence Signals vs. Temperature Variation (upper(a); at 21℃, middle(b); at 37℃, *lower(c); at 55℃*)

at time zero of three fluorescence signals is the same, but the lifetime of each is shortened by the addition of quenchers(Mn^{2+} or Ca^{2+}). This method has an error range within ±2% for the two samples with quenchers and is useful for monitoring of real-time uranium concentration on

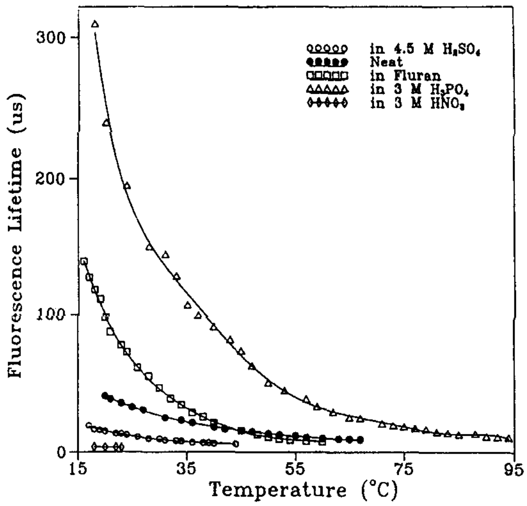

Fig. 7. Fluorescence Lifetime Change According to Temperature Change on Aqueous Solution

the raw solution which has the various quenchers.

3.1. Temperature fluctuation

The lifetime of uranium fluorescence appears to be considerably shortened by the increase of temperature. This is considered to be due to the serious quenching caused by frequent collisions at higher temperature. Fig. 6 shows the signals of uranium fluorescence on the aqueous solution(1 ppm UO_2^{2+}, pH=6) measured at 21℃, 37℃, 55 ℃, respectively. The lifetime of fluorescence at 21 ℃ is three times compared with that at 55℃. The fluorescence intensity of these three signals at time zero is the same irrespective of temperature fluctuation. This method analyzed by the use of fluorescence intensity at time zero has the error range within 6% at temperature from 19℃ to 45℃ The error range from temperature fluctuation is larger than that from quenchers. It is considered to be due to the use of the fixed gate and delay intervals in spite of serious lifetime fluctuation. It is difficult to get precise fluorescence intensity at

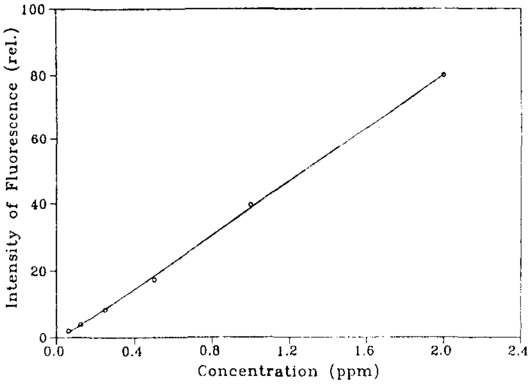

Fig. 8. Linearity of Fluorescence Intensity Change vs. Uranium Concentration Change

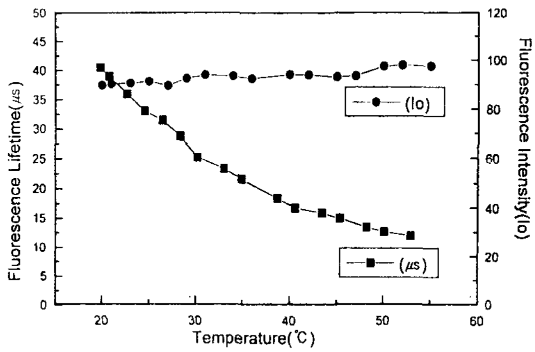

Fig. 9. Change of Uranium Fluorescence Lifetime (μs) and Variation of Fluorescence Intensity(I_0) at Time Zero with Respect to Temperature

time zero with the fixed gate interval of 7μs and the fixed delay interval of 10μs at the temperature of over 45℃ caused by the increase of error rate at S_2 value due to the shortened lifetime[11].

Fig. 7 shows the variation of fluorescence lifetime vs. the temperature change on the various solutions. The problem of fluorescence lifetime change according to temperature variation on the four sample solutions is considered to be serious. The temperature fluctuation should be considered for detection of the remote real-time uranium concentration without sample preparation because the change of uranium fluorescence lifetime is large compared with small temperature change. The method using fluorescence intensity at time zero is free from the effect of quenchers and temperature fluctuations within 10℃ range of the room temperature.

3.3. Detection Limit, Linearity and Error Range

The test for the remote real-time uranium fluorimeter was accomplished with the two optrodes which had the ability to shield external light source or not. The fluorescence intensity obtained from two optrodes on the same sample without external light were same and good for uranium detection. Fig. 8 shows the calibration curve of the fluorescence intensity vs. uranium concentration. The linearity is excellent within the range of 0.06 ppm to 2 ppm of uranium sample at room temperature. The detection limit is 0.06 ppm. The detection limit can be lowered by the use of a strong light source and by the control of the focusing angle of uranium fluorescence generated by laser beam.

Fig. 9 shows change of uranium fluorescence lifetime(μs) and variation of fluorescence intensity(I_0) at time zero deriving with this apparatus with respect to temperature between 20℃ and 55℃. As a result, this apparatus for monitoring real-time uranium concentration applied the method using fluorescence intensity at time zero has relatively good error range within ±6% irrespective of the effect of quenchers or temperature fluctuation.

4. Conclusions

An apparatus for detecting remote real-time uranium concentration using the optrode was developed. The optrode composed of a concave mirror, Duralumin structure and optical fibers was designed. The derivation method of fluorescence intensity at time zero to exclude the effect of quenchers and temperature fluctuations for more precious analysis was employed. At a result, this uranium fluorimeter has an error range within 6% in spite of serious lifetime change due to quenching effect and temperature fluctuations. The detection limit is 0.06 ppm and the linearity is excellent between 0.06 ppm and 2 ppm on aqueous solution(pH=6). This apparatus could be applied for monitoring remote real-time uranium leakage in the cooling and condensation water of the reprocessing process.

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