

Study on the Characteristics of Laser-induced Fluorescence from Trace Samarium, Europium and Terbium

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미량분석을 위한 Sm, Eu와 Tb의 레이저 여기 형광 특성 분석

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Abstract

The purpose of this study was to develop a rapid and effective method of laser-induced fluorescence analysis for trace amounts of Sm, Eu and Tb in nuclear fuels. The features of the method are the use of the distinct fluorescence wavelengths and the discriminative lifetimes of the respective elements when excited by a pulsed nitrogen laser. Fluorescence signals of the three elements were isolated by adequate selection of the filters or complexing agents (HFA, TTA) or discriminative delay and gate times in the signal processing circuit. It was found that Sm^{+3} and Eu^{+3} emitted strong fluorescence in the two complexing agent solutions of HFA and TTA. But in the case of Tb^{+3} , the fluorescence signal was detected only in HFA solution. With respect to the concentrations of Sm^{+3} , Eu^{+3} and Tb^{+3} , the fluorescence signal intensities gave superior linearities in the range of 5 ppb-10 ppm for Sm^{+3} , 0.5 ppb-1 ppm for Eu^{+3} , and 0.1 ppb-300 ppb for Tb^{+3} . The detection limits obtained were 5 ppb for Sm^{+3} , 0.1 ppb for Eu^{+3} , and 0.01 ppb for Tb^{+3} , respectively.

요 약

본 연구에서는 소형 펄스 질소 레이저를 여기 광원으로 사용하여 Sm, Eu 및 Tb를 각각에서 나오는 독특한 형광 파장과 lifetime 차이를 이용하여 효과적으로 정량 분석할 수 있는 방법을 연구하였다. 적절한 complexing agents(TTA 또는 HFA)와 band-pass filter에 의한 형광 파장 선택과 신호 처리 부분에서의 형광 lifetime 차이를 고려한 delay time과 gate time의 조절에 의해 형광 신호를 처리함으로써 상호 분리분석이 가능하였다. Sm^{+3} 과 Eu^{+3} 의 경우 두 complexing agents 용액 모두에서 5ppb-10ppm 및 0.5ppb-2ppm 범위에서 농도에 대한 intensity의 직선성이 우수하였고, Tb^{+3} 의 경우는 HFA complexing agent 용액에서만 0.1ppb-300ppb 범위에서 직선성이 우수하였다. 검출한계는 Sm^{+3} 의 경우 5ppb, Eu^{+3} 의 경우 0.1ppb, Tb^{+3} 의 경우 0.01ppb의 매우 낮은 값을 나타내었다.

I. Introduction

Trace amounts of rare earth elements including, Sm, Eu and Tb, etc., exist in nuclear fuel and are very contaminating to the fuel because of their large thermal neutron absorption cross sections¹⁾. Rare earth elements are also present in Zircaloy with a total concentration of 1 ppm or below. Several different methods of trace analysis of rare earth elements in the nuclear industry have been developed for several decades in the light of nuclear fuel qualification.

Primarily, emission spectrography^{2,3)} and X-ray fluorometry⁴⁾ have been used for analysis of rare earth elements. But these methods not only involve somewhat complex analytical processes, but are rather costly. Also, these methods generally show higher detection limits of over several tens of ppb and are tediously time consuming. The instruments for the conventional methods are also too heavy and large to transport for field measurement. Recently, however, with the development of lasers, analytical techniques using lasers have played an

PMT: photomultiplier tube (HAMAMATSU type 1P28A)

Cell : quartz cell (size: 10 mm × 10 mm × 40 mm)

L : quartz biconvex lens (L1:f=7.5 cm, L2:f=4.5 cm)

N₂ Laser: Model VSL-337, 120 μ J/pulse, pulse width (FWHM): <3 ns.

important role in the analyses of trace metallic elements⁵⁾. Especially, laser fluorometry has been widely used because of its compactness, high selectivity and low detection limit.

The laser-induced fluorescence analyzer developed in KAERI for trace uranium analysis has already shown good analytical features, such as relatively simple analytical procedures over conventional methods and very low detection limit of below 0.1 ppb⁶⁾. The same instrument has been used for the analysis of rare earth elements, and to this point, Sm⁺³, Eu⁺³ and Tb⁺³ have been successfully analyzed.

II. Experimental

1. Apparatus

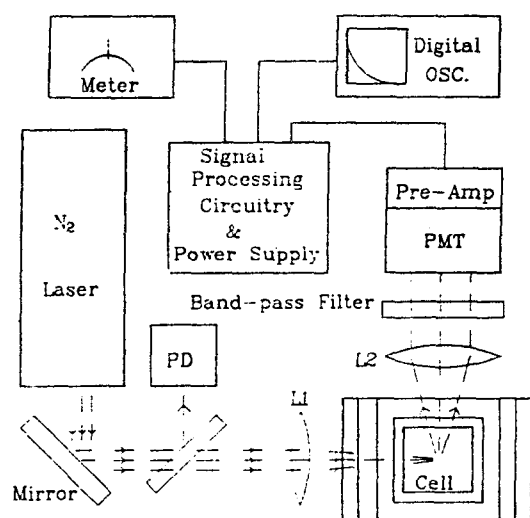


Fig. 1. Schematic Diagram of Fluorescence Analyzer System

Fig. 1 shows a schematic diagram of the fluorescence analyzer used for this study. The principles of this method and the detailed explanation of fig. 1 have been described previously⁶⁻⁸⁾. A N₂ laser (Laser Science Inc. Model VSL-337) used as an excitation light source gave a pulse width of less than 3 ns (stated value). This value and other electronic processing times seemed sufficiently short to measure the time evolution of fluorescence signal for lifetime measurement. Because of distinct fluorescence spectra of the respective elements, different band-pass filters should be used for wavelength selection (Sm:555-565 nm, Eu:606-616 nm, Tb:480-550 nm). Delay and gate times could be controlled from several μ s up to 10 ms

in the electronic circuit so as to discriminate different fluorescence lifetimes. The short-lived fluorescence signals from various organics or different components could be eliminated by controlling the delay time. The signals within gate time were integrated. To compensate for the fluctuations of laser output power ($\pm 3\%$), signal intensities of about 50 cycles were accumulated.

2. Reagents and Experimental Procedures

The primary 1,000 ppm stock solutions of Sm^{+3} , Eu^{+3} and Tb^{+3} were prepared as dissolving the reagent-grade oxide compounds in concentrated HCl. These were diluted with distilled water to use as standard samples. One complexing agent solution was prepared as dissolving 6×10^{-4} M TTA (Thenoyl Trifluoroacetone) in methylcyclohexane and the other as dissolving 6×10^{-4} M HFA (Hexafluoroacetylacetone) in methylcyclohexane. The synergic agent of TOPO (Tri-*n*-octyl Phosphine Oxide) solution was prepared as dissolving 0.01 M TOPO in methylcyclohexane⁹⁾.

The experimental procedures were as follows; 3 ml either Sm^{+3} , Eu^{+3} or Tb^{+3} standard solutions, 3 ml of acetate buffer (pH 4.76) and 3 ml of synergic solution were added to the 3 ml of organic complexing agent solution in the test tube. These solutions were thoroughly shaken for 15 seconds. The organic upper layer was transferred with a micropipet to the 10 mm \times 10 mm \times 40 mm quartz fluorescence cell. The laser fluorometer was calibrated with a blank solution which was prepared through the above mentioned procedures except using distilled water instead of standard sample solution.

3. The Fluorescence Spectra of Sm^{+3} , Eu^{+3} and Tb^{+3}

The fluorescence emission spectra of Sm^{+3} , Eu^{+3}

and Tb^{+3} , excited at 337.1 nm, were obtained by scanning from 400 nm to 650 nm with a JOBIN YVON, Model JY3 fluorometer. The Sm^{+3} showed three strong fluorescence signals at 563 nm, 600 nm and 640 nm, and Eu^{+3} showed a single peak at 612 nm in both of the two complexing agent (HFA, TTA) solutions. But in the case of Tb^{+3} , the fluorescence signal was detected only in HFA solution at 491 nm and 546 nm. We used these data to select the wavelength band-pass filter for fluorescence discrimination of each element.

4. The pH Dependence of the Fluorescence Signals

The fluorescence intensities with respect to pH variation were measured. In this experiment, we used the complexing agent TTA for Sm^{+3} and Eu^{+3} , and HFA for Tb^{+3} . At the sacrifice of the buffer capacities, only the acetate buffer ($\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$) was used through the pH ranges due to the reduction of the expected various anion interferences. In fig. 2, Sm^{+3} and Eu^{+3} show strong and near constant fluorescence signals in the region of pH 3-7, but rapid decay appears below pH 3 and above pH 7.5. In the case of Tb^{+3} , fluorescence is strong in the region of pH 3-6 but decay appears below pH 3 and above pH 6. It could be noted that pH variation strongly affected the extraction efficiencies of the sample elements to the organic solution. These pH dependences are due to the facts that; (1) at low pH values, hydronium ion competition with rare earth ions for an enolate group in complexing agents (HFA, TTA) should reduce extraction efficiency, while (2) at high pH, the rare earth ion should form hydrated hydroxides rather than chelate complexes with the complexing agents (HFA or TTA)¹⁰⁾. Thus, we performed all the experiments at pH 4.76.

III. Results and Discussion

1. The Fluorescence Signal Discrimination Using Band-pass Filter and Lifetime Measurement

Fig. 3 shows fluorescence signals of Sm^{+3} at pH 4.76, and a lifetime of about 70 μs in both TTA and HFA complexing agent solutions. The

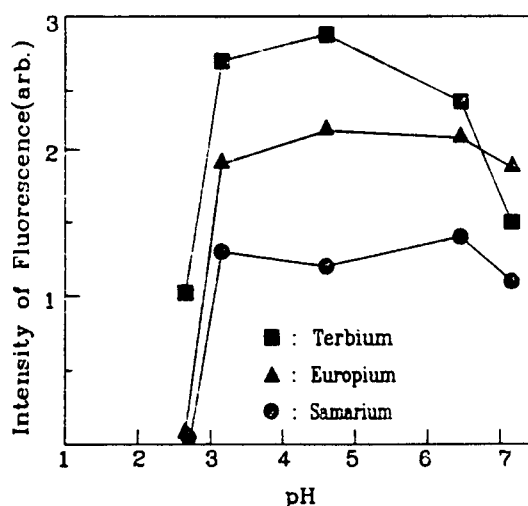


Fig. 2. The Fluorescence Intensities of Sm^{+3} , Eu^{+3} and Tb^{+3} with respect to the pH Variation in Acetate Buffer ($\text{CH}_3\text{COO Na} + \text{CH}_3\text{COOH}$)

- : Sm (in TTA/TOPO-Methylcyclohexane)
- ▲: Eu (in TTA/TOPO-Methylcyclohexane)
- : Tb (in HFA/TOPO-Methylcyclohexane)

fluorescence signals of Eu^{+3} are also presented in fig. 4. The lifetime of Eu^{+3} is shown to be about 0.7 ms. It is noted that the fluorescence lifetime of Eu^{+3} is 10 times as long as that of Sm^{+3} . Fig. 5 shows the fluorescence signal of Tb^{+3} . The signals were detected only in HFA complexing agent solution with a lifetime of about 40 μs . For all the fluorescence signal measurements, LeCroy 9400 storage oscilloscope (bandwidth; 125 MHz)

was used. To measure the fluorescence signal of Eu^{+3} in the mixture of Sm^{+3} and Eu^{+3} , using a 606.5-616.5 nm band-pass filter, it would be difficult to distinguish the signals from which it was emitted. This is because fluorescence wavelengths of Sm^{+3} and Eu^{+3} are slightly overlapped. But using the great differences of fluorescence lifetimes, the analysis of fluorescence signals between Sm^{+3} and Eu^{+3} could be easily performed. For example, at 0.4 ms of delay time and 1 ms of gate time, the ratio of integrated fluorescence intensity, ($I_{\text{Sm}}/I_{\text{Eu}}$), was about 1/70. Thus, the accurate analysis of the signal from Eu^{+3} was possible. The fluorescence of Sm^{+3} could be easily detected only by using a 555-565 nm band-pass filter. This is because Eu^{+3} has no emission peaks in this wavelength region.

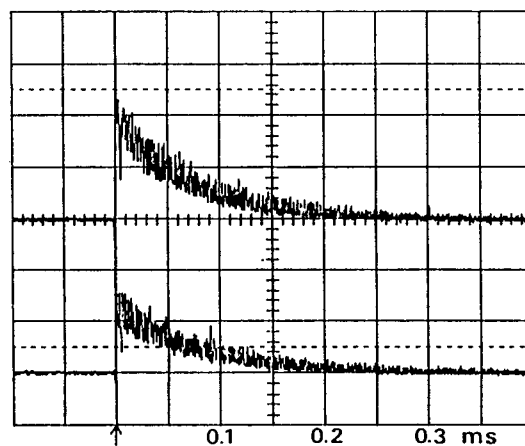


Fig. 3. Fluorescence Signal of Sm^{+3}
in HFA/TOPO-Methylcyclohexane (Upper)
in TTA/TOPO-Methylcyclohexane (Lower)

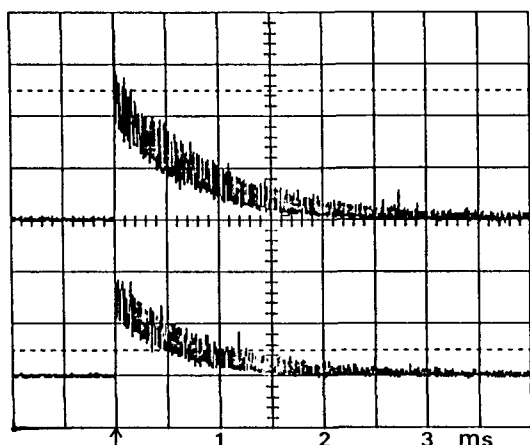


Fig. 4. Fluorescence Signal of Eu^{+3}
in HFA/TOPO-Methylcyclohexane (Upper)
in TTA/TOPO-Methylcyclohexane (Lower)

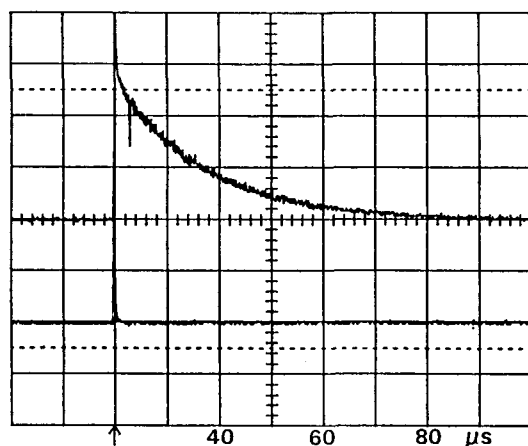


Fig. 5. Fluorescence Signal of Tb^{+3}
in HFA/TOPO-Methylcyclohexane (Upper)
in TTA/TOPO-Methylcyclohexane (Lower)

In all the cases above, the fluorescence signals using HFA complexing agent solution were more intense than those using TTA complexing agent solution. The fluorescence signals of Sm^{+3} and Eu^{+3} were found to be about 1.5 times more in-

tense in HFA complexing agent solution. Furthermore, the signal of Tb^{+3} was detected only in HFA solution. The absence of the fluorescence of Tb^{+3} in TTA complexing agent solution seemed to be a result of the fact that no fluorescing chelate could be formed between Tb^{+3} and TTA⁽¹¹⁾. Therefore, it will be more useful to use HFA instead of TTA for obtaining lower detection limit of the sample elements, Sm^{+3} , Eu^{+3} , and Tb^{+3} .

For the analyses of trace amounts of rare earth elements in nuclear fuels, the following analytical scheme as in fig. 6 could be recommended.

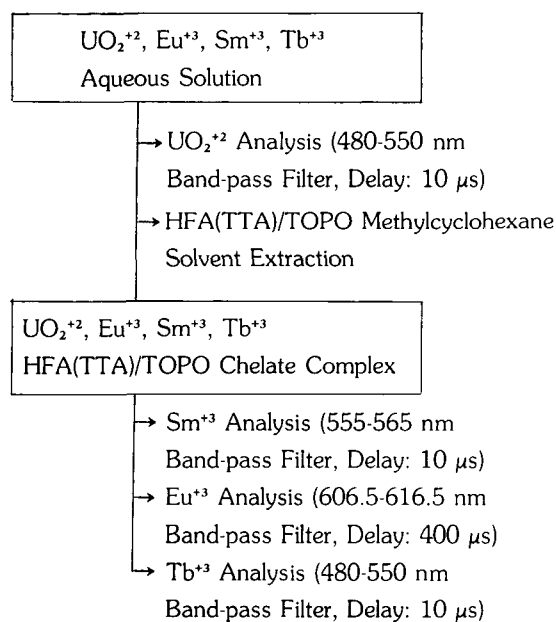


Fig. 6. Analytical Scheme for a Sample Mixture of U, Sm, Eu and Tb

2. Calibration of the Signal Intensities with Respect to the Sample Concentrations

Fig. 7 shows the correlations of fluorescence intensities with respect to the concentrations of Sm^{+3} , Eu^{+3} and Tb^{+3} . Eu^{+3} and Sm^{+3} were measured in TTA complexing agent solution, and

Tb³⁺ in HFA complexing agent solution at pH 4.76. The linearities were good in the broad range of concentrations, i.e., 5 ppb-10 ppm for Sm³⁺, 0.5 ppb-2 ppm for Eu³⁺, and 0.1 ppb-300 ppb for Tb³⁺, respectively. Thus, it is possible to analyze Sm³⁺, Eu³⁺ and Tb³⁺ quantitatively in the broad concentration ranges.

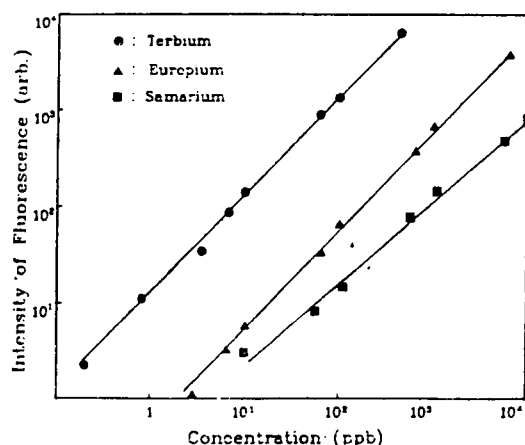


Fig. 7. Calibration Curves of Sm³⁺, Eu³⁺ and Tb³⁺ with respect to the Concentrations.

Sm³⁺ and Eu³⁺ were measured in TTA complexing agent solution and Tb³⁺ was measured in HFA complexing agent solution using acetate buffer at pH 4.76

IV. Conclusion

A rapid and more exact analytical method for trace analysis of rare earth elements, such as Sm³⁺, Eu³⁺ and Tb³⁺, was studied using a pulsed N₂ laser. The laser-induced fluorescence signals from the sample elements were discriminated according to their different specific fluorescence wavelengths and their respective lifetimes. Because the feature of the method was to use the differences of wavelength and those of the lifetimes simultaneously, we were able to reduce many problems caused due to the overlapping

of fluorescence wavelengths of different sample elements. The experimental results using N₂ laser-induced fluorometry for the analysis of rare earth elements, Sm³⁺, Eu³⁺ and Tb³⁺ were as follows:

1. In the mixture of Sm³⁺ and Eu³⁺, Eu³⁺ could be analyzed making use of its extreme lifetime difference from Sm³⁺. (Sm³⁺; 70 μ s, Eu³⁺; 0.7 ms), and Sm³⁺ could be analyzed making use of its specific fluorescence wavelength emitted at 560 nm.
2. Tb³⁺ could be analyzed using fluorescence signals, emitted at 491 nm and 546 nm, which were transmitted through a green filter (480-550 nm). However, for the nuclear fuel qualification, UO₂⁺² exist in the sample solution and a severe interference from UO₂⁺² would be expected due to its green fluorescence (491 nm, 516 nm, 540 nm). The UO₂⁺² fluorescence, which has been detected in aqueous nitrate solution, was not detected in either the HFA or TTA complexing agent solutions. Therefore, it would be possible to analyze the fluorescence from UO₂⁺² by using aqueous nitrate solution and that from Tb³⁺ by using HFA complexing agent solution.
3. The detection limits obtained as S/N ratio of 2 were 5 ppb for Sm³⁺, 0.1 ppb for Eu³⁺, and 0.01 ppb for Tb³⁺, respectively.

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