

Trace Analysis of Uranium in Aqueous Samples by Laser-induced Fluorescence Spectroscopy

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(Received July 31, 1987)

레이저를 이용한 용액중의 미량 우라늄 분석

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(1987. 7. 31 접수)

Abstract

A sensitive, direct method for the determination of trace amounts of uranium in solution has been developed utilizing laser-induced fluorescence spectroscopy and a fluorescence enhancing reagent 'Fluran.' Standard addition technique is incorporated into the analysis to eliminate sample matrix effects. Analytical data show that a detection limit of 0.1 ppb (part per billion) uranium has been achieved and the precision of the analysis is in the range of $\pm 5\%$ relative standard deviation. Results using the laser fluorescence method on many sets of unknown samples have been compared against corresponding values determined by other methods.

요 약

레이저를 이용한 형광분석 방법과 형광의 세기를 증대시켜주는 'Fluran' 용액을 가함으로써 용액 속에 존재하는 미량의 우라늄을 정확하고 신속하게 분석할 수 있는 새로운 장치를 개발하였다. 표준 용액의 첨가 방법을 이용하여 시료의 조성 변화에 따른 형광의 방해효과를 보정할 수 있었고 5% 이내의 정밀도를 갖는 0.1ppb의 측정 하한치를 얻을 수 있었다. 또한 여러 종류의 시료에 대하여 레이저를 이용한 형광분석 방법의 결과와 다른 측정 방법에 의한 결과를 상호 비교, 분석하였다.

I. Introduction

There is considerable interest in the determination of trace quantities of uranium. In geochemistry, a continuing effort has been directed to the uranium exploration, where large areas must be covered quickly and economically. In the process control, it is important to monitor the accurate uranium content for the economic extraction of uranium from solution by the

general extraction process. Routine urinalysis for uranium has been used to monitor protection measures so that workers who might inhale airborne yellowcake dust do not accumulate dangerous amounts of internally deposited uranium. Furthermore, monitoring of uranium in waste waters from mining or millsite installations could be useful for environmental protection since radioactive products from uranium such as radium and radon are hazardous if they enter the water supply. As such investigations require

analysis of large number of samples, it is necessary to use a fast, simple and accurate determination method.

Of the methods used to determine trace quantities of uranium, the most common and sensitive method is the measurement of its fluorescence⁽¹⁾. Uranium fluorescence has been measured in liquid media such as sulfuric and phosphoric acid, or in disks or pellets after fusion with salts such as sodium fluoride or carbonate. Fusion methods are preferred over solution techniques because of their relatively better sensitivity and specificity, and have been used extensively since the early 1950's^(2,3). But many factors affect its fluorescence intensity in fused pellets. For example, the fusion requires strictly regulated conditions of flux composition, heating time, and temperature. The method is time consuming, usually involving separation to remove interfering elements. Other analytical techniques with sufficient sensitivity for measurement of uranium in natural water include neutron activation⁽⁴⁾, fission track⁽⁵⁾ and optical fluorimetry⁽⁶⁾. None of these methods can be regarded as a field technique due to the need for access to either laboratory or reactor facilities.

The application of laser-induced fluorescence for the uranium detection has been investigated recently⁽⁷⁻¹⁰⁾. A sensitive technique has been developed in this laboratory⁽¹¹⁾ with a detection limit of 0.1 ppb U based on direct measurement of the fluorescence intensity of uranyl ions in aqueous solution excited by a pulsed nitrogen laser.

The principles of the method have been described in detail previously⁽¹¹⁾, so we will give only a very short survey. Under ultraviolet excitation, which in the present technique is provided by a small nitrogen laser(337nm), solution containing uranyl ion, UO_2^{2+} , emits green fluorescence that can be measured quantitatively by a suitable photodetector. The emission

spectrum is quite characteristic, with three regularly spaced peaks. As any fluorescence from organic matter in the solution is superimposed on the uranium fluorescence, a discrimination by time and wavelength is provided. On excitation, most natural waters show a quite intense blue fluorescence with a maximum intensity which is probably around 400nm. Radiation of this wavelength can be blocked by a green filter used for isolation of the uranium fluorescence. After excitation by laser pulse, fluorescence of most organic molecules does in fact decay very rapidly; lifetimes are measured, at most, as some few tens of nanosecond. In contrast, the fluorescence of uranyl ion persists for a comparatively long time; its lifetime is typically some few tens of microsecond. Triggered by the laser, an electronic delaying gate accepts signals only after the fluorescence from the organics has substantially decayed and integrates uranium fluorescence during gatetime, thus achieving an almost complete isolation of the uranium contribution. To improve stability, the outputs from about 50 cycles are accumulated.

In order to increase the uranium fluorescence intensity, 'Fluran' (Scintrex Limited, Canada) is added to the test sample. The primary function of the Fluran solution is the formation of a single fluorescent uranyl species⁽¹²⁾, but it also acts as a strong complexing agent for other metals in solution to reduce their interference effects on uranyl fluorescence. Fluran contains a buffer to maintain optimum pH for both fluorescence and masking efficiency.

II. Experiment

II. 1. Apparatus

A schematic layout of the uranium analyser is shown in Fig. 1. The instrument employs a compact sealed nitrogen laser (Laser Science Inc. VSL-337) which emits ultraviolet pulses at

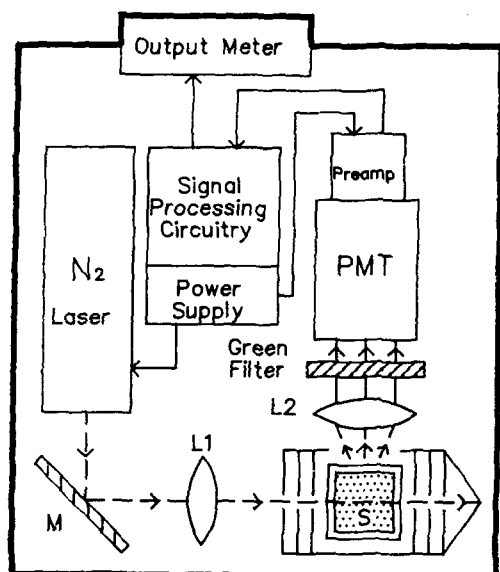


Fig. 1. Schematic Diagram of the Experimental Apparatus.

repetition rate of 10 pulses per second. A laser is used in preference to other sources of ultra-violet light because the resultant pulse is intense, self-terminating, monochromatic and highly directional; the full output power of 40 KW and 3ns pulse is thus easily directed and focused using mirror(M) and lens(L₁) on the sample cell(S). The fluorescence of a solution in the cell is collected using lens L₂ and detected by a Hamamatsu 1P28A photomultiplier (PMT) isolated by a green-transmitting filter (Melles Griot 03FIA003; 490<λ<580nm). The amplified and gated fluorescence intensity signals from the PMT are integrated for 50 pulses and then displayed on a panel meter which can be converted directly to uranium concentration. A 125-MHz digital oscilloscope (Lecroy 9400) was used in detecting the time-dependent fluorescence intensity signal. The response time of fluorescence detecting electronic circuit was 1μsec.

The sensitivity of the instrument is adjusted by varying photomultiplier tube gain and an three (×1, ×10, ×100) range switch is provided to enable wide range of uranium levels

(0.1~500 ppb) to be measured directly. When the concentration of a sample is higher than a selected range, an overload light and pulse counting LED blink, which indicates a dilution is required to bring the concentration within range. For all measurements, small amount of samples (2.5ml) was used in a standard quartz rectangular cell of 1×1×4cm. The dimension of the instrument is 40×45×17cm; the weight is 15kg. The power consumption of the instrument is about 25 watts at 110 volts; when required, the source may be a DC 12 volt battery.

II. 2. Standard Addition Technique

The addition of a known amount of uranium to a sample and the observation of the response from that standard provide an easy method of accounting for any interferences in the samples. This is done by adding a small volume (i.e. 5~50μl) of a uranium standard to a sample following normal analysis and noting the upscale deflection. In this case the response due to the standard will be the difference between the reading of sample only and the reading of sample plus standard. The uranium concentration of a sample is calculated as follows:

$$\frac{RES_{spl}}{RES_{spl+add} - RES_{spl}} \times \frac{VOL_{add}}{VOL_{spl}} \times \frac{1}{DIL_{spl}} \times CONC_{std}$$

where

RES_{spl} = response of the sample

RES_{spl+add} = response of the sample plus standard added

VOL_{add} = volume of the standard addition

VOL_{spl} = volume of the sample solution

CONC_{std} = concentration of the standard

DIL_{spl} = dilution ratio of the sample.

The amount of standard added should be chosen so that there is a significant upscale to avoid meter reading errors.

II. 3. Uranium Standard Solutions

The primary 1,000ppm U standard solution was prepared by dissolving the reagent grade

uranyl nitrate (B.D.H. Chemical Ltd.) in 5% nitric acid (2.11g $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per liter). This was diluted 100 times and a further 10 times to form 10ppm (in 0.05% HNO_3) and 1ppm (0.005% HNO_3) respectively. Acid has been added to standards diluted below 1ppm U to keep total acid concentration around 0.005%. Very dilute standards in very pure water (at pH7) sometimes exhibit some fluorescence⁽¹³⁾ even without the addition of Fluran. Slight acidification suppresses the fluorescence and also contribute to improve stability of the standard. The dilute standards containing ppb U have been made up daily.

III. Result and Discussion

The fluorescence emission spectrum of uranium in solution as measured by the laser-induced fluorescence spectroscopy is shown in Fig. 2. This spectrum was obtained from wavelength scanning using a monochromator following excitation of aqueous uranyl nitrate solution with

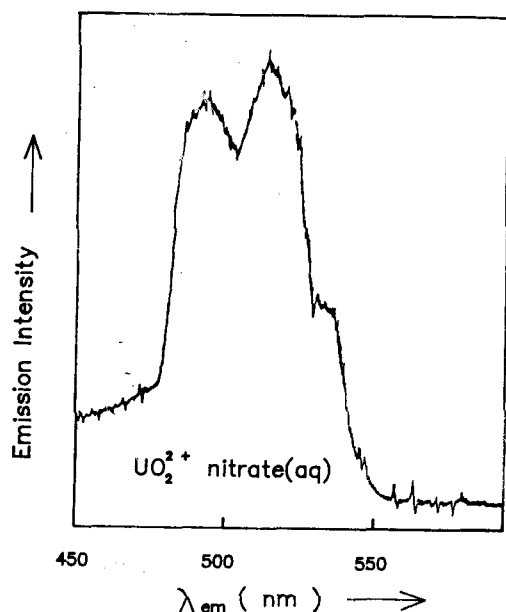


Fig. 2. Fluorescence Spectrum of 0.04M Uranyl Nitrate Solution Excited at 337nm.

nitrogen laser at 20Hz repetition rate. Three peaks at the wavelengths of 494, 516 and 540nm characterize the uranium fluorescence. Similar results were published by Kenney-Wallace et al.⁽¹⁴⁾. This result would lead a conclusion that the quantitative measurement of uranium in solution can be obtained from distinctive fluorescence intensity using a wavelength discrimination.

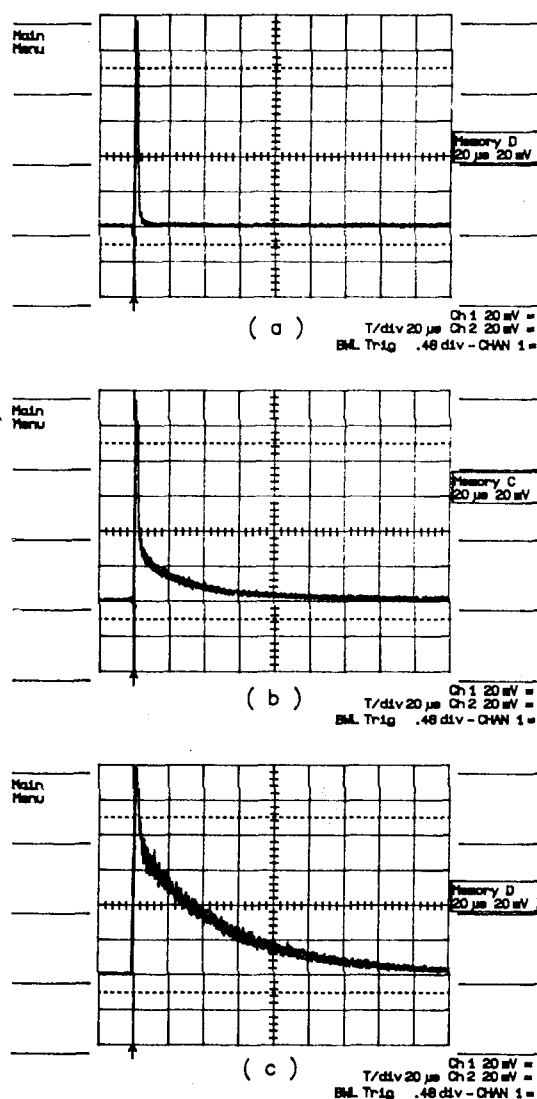


Fig. 3. Fluorescence Lifetimes of Laser-induced Emission:

- a) blank solution;
- b) 100ppb uranium solution;
- c) 100ppb uranium and Fluran solution.

The radiative lifetimes of the laser-induced emission were measured for blank and uranium in solution. Following laser excitation, the relatively long-lived green emission could be readily observed. The oscilloscope traces in Fig. 3-a, b show typical emission signals of blank and 100ppb U solution following nanosecond laser excitation at room temperature.

The fluorescence of 100ppb U solution decays exponentially with a lifetime of about $20\mu\text{sec}$. In contrast, the fluorescence of blank solution decays with a lifetime less than $3\mu\text{sec}$. Above results show that the interference of short-lived fluorescence could be eliminated by detecting the long-lived component after an appropriate delay time following excitation cut-off.

Fig. 3-c shows that the fluorescence intensity and lifetimes in aqueous solution were all remarkably enhanced upon addition of Fluran. For example, $\tau=20\mu\text{sec}$ for uranyl nitrate solution increases to $\tau=40\mu\text{sec}$ in the presence of Fluran. Fluran is a compound of a chelating agent and a fluorescence enhancing agent⁽¹²⁾ which, because of the high stability constant of its uranyl ion complex, guarantees that the fluorescence mea-

sured always comes from the same species. As the stability of the complex is PH-dependent, Fluran also contains sufficient amount of phosphate buffer (pH=7).

Fig. 4 shows the dependence of the signal on the amount of Fluran added, at a 0.1ppb U concentration. The uranium fluorescence intensity increases with increasing Fluran to a maximum at 0.4ml. For higher uranium concentrations the curve shape does not change. From the results obtained it can be concluded that the optimum Fluran volume is 0.4ml when the sample volume is 2.5ml.

Fig. 5 shows the calibration curve, obtained under the optimized experimental condition with a standard solution of uranyl nitrate. A major feature of this experiment is the use of the standard addition technique (the addition of a known amount of uranium standard to the solution being measured) to correct the effect of interferences. The measured curve was linear for the range of 0.1~500ppb uranium and the detection limit (2 times the standard deviation of the background signal) was 0.1ppb.

A primary evaluation of the laser-induced

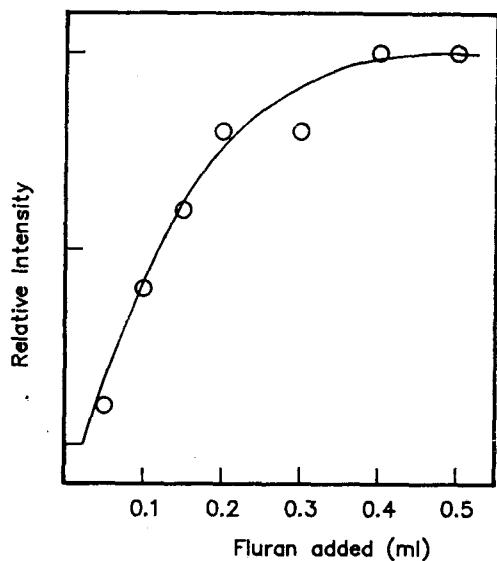


Fig. 4. Dependence of the Signal Intensity on Amount of Fluran Added.

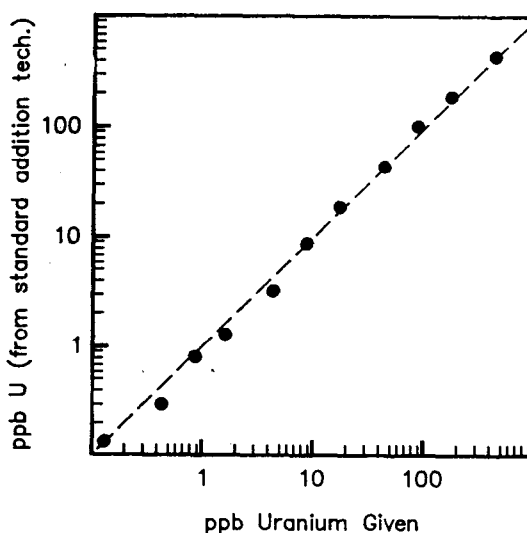


Fig. 5. Calibration Curve of Uranium by Standard Addition Method.

fluorometric method versus the fused-disk fluorometric^(2,3) and spectrophotometric⁽¹⁵⁾ method was made over the concentration range of 100ppb to 250ppm of unknown sample solution with different matrices. A scatter diagram relating uranium concentrations in four sets of solutions was determined from the laser-induced fluorometric technique and the corresponding measurements made on the same samples from independent laboratory using different techniques. Perfect correlation ($r=1$) would show all data points lying on a line passing through the origin at 45 degrees to the major axes; scatter of points about such a line indicates a lower degree of correlation. As shown in Fig. 6 and Fig. 7, good correlation (r greater than 0.98) has been obtained on all sets of samples tested to date, which now include a different solution matrices and concentrations.

The measurement for uranium in 0.18M H_3BO_3 exhibits a small difference between two methods. This result may be interpreted in terms of the interference effects⁽¹⁶⁾ of concentrated H_3BO_3 which is serious in the fused-disk fluorometric method, thus obtaining a lower values

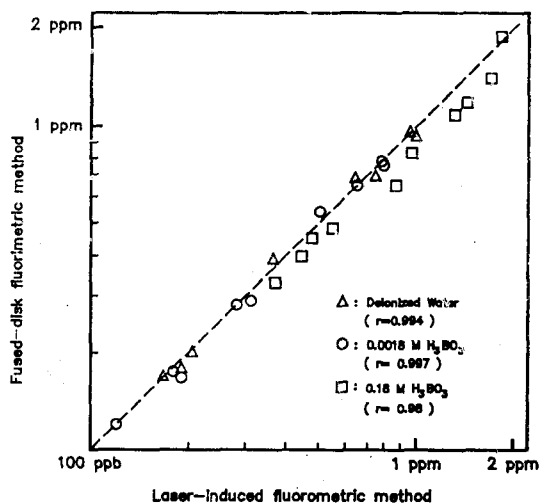


Fig. 6. Correlation Plot of Fused-disk Fluorometric Analysis vs. Laser-induced Fluorometric Method for Uranium in Various Solutions.

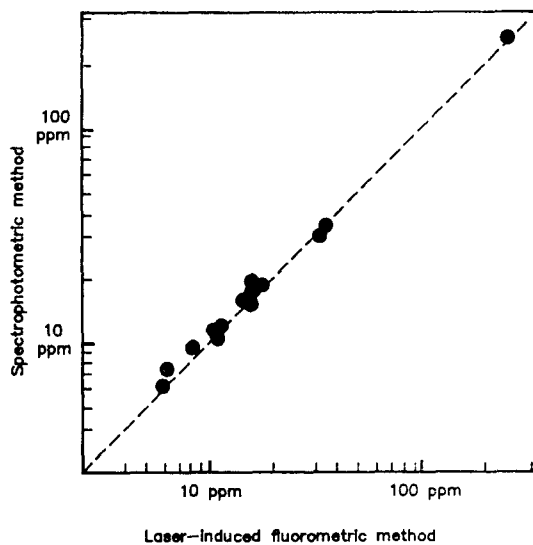


Fig. 7. Correlation Plot of Spectrophotometric Analysis using Arsenazo-III vs. Laser-induced Fluorometric Method for High Level Uranium.

than laser-induced fluorometric method.

Comparing with other two techniques, the laser-induced fluorometric method uses fewer steps giving results in less time. A significant advantage of this instrument is that a uranium standard can be added directly to the sample. This method recalibrates the instrument in a very easy manner for each measurement. Summarizing, laser-induced fluorometry can be recommended for the determination of uranium concentrations when the number of samples is very large.

IV. Conclusion

The fact that with a pulsed nitrogen laser we can now selectively excite the uranium in solution leads immediately to the conclusion that this is a powerful analytical method for the determination of trace uranium. The following conclusions were reached from this study:

1. Accuracies of the order of $\pm 5\%$ can be expected over the range of 0.1~500ppb U, if

adequate care is taken in the dilution of the original samples.

2. The time per analysis with this instrument (30 samples per hour) appears to be significantly shorter than the conventional methods.

In addition, it appears feasible to adapt this instrument to a fully automatic on-stream analysis. Such an on-stream analyser would have numerous advantages in process control and cost saving.

Our instrument is light in weight, small in size, and of low power consumption. It is ruggedly built, being intended for transportation into remote areas to provide a uranium analytical facility for geochemical analysis of waters, soils or rocks for uranium extraction purposes. Whether used in a remote location or permanent laboratory, immediated and accurate measurements with a sensivity of 0.1ppb U can be made. Thus, this instrument has applications in geochemical exploration, pollution surveillance and process control

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