UCID-17549

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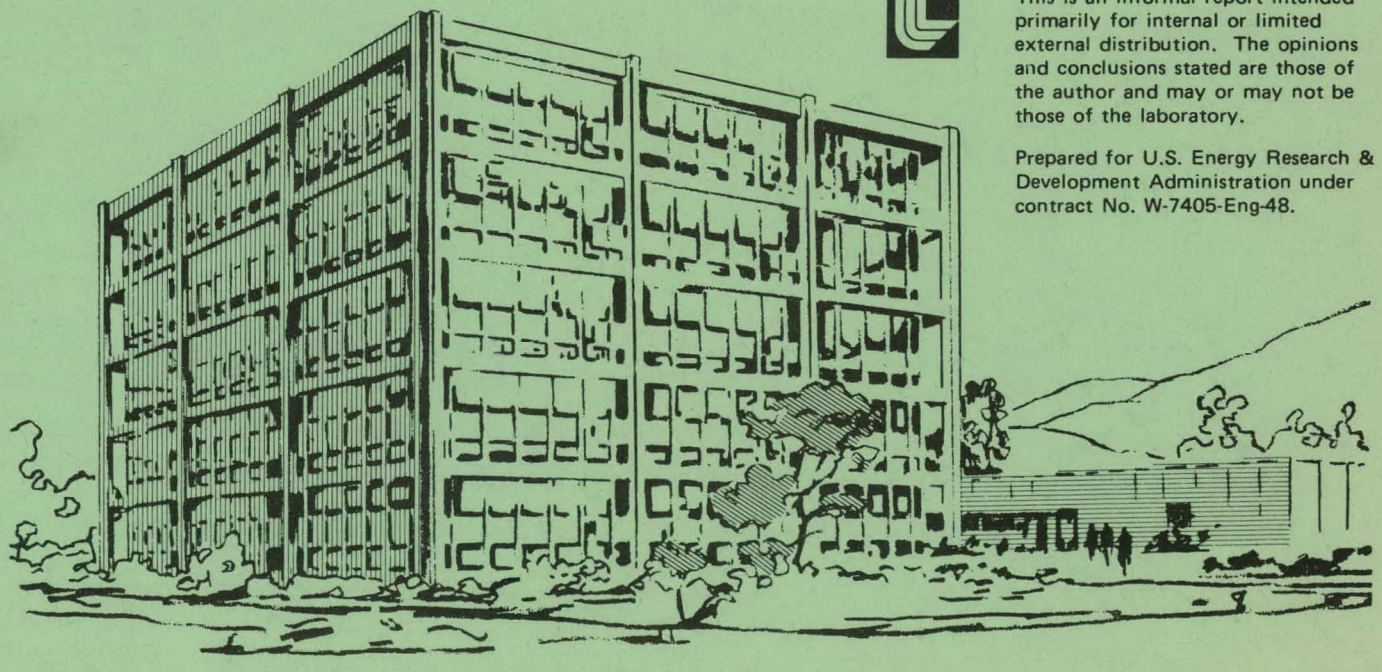
TRACE URANIUM - ITS MEASUREMENT BY TIME-RESOLVED FLUORESCENCE

F. B. Stephens, G. R. Haugen and J. H. Richardson

July 15, 1977



Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

DISCLAIMER

TRACE URANIUM - ITS MEASUREMENT BY TIME-RESOLVED FLUORESCENCE

F. B. Stephens, G. R. Haugen and J. H. Richardson
University of California
Lawrence Livermore Laboratory
Post Office Box 808
Livermore, California 94550

Abstract

An investigation was undertaken to extend the limits of detection of uranium in natural waters to the parts-per-trillion (10^{12}) level using a laser-induced fluorescence technique.

Observations of the time-resolved fluorescence spectrum were made using two techniques - boxcar integration and a pulse counting technique. Neither technique provided greater sensitivity into the parts-per-trillion range. This has been attributed to the long fluorescence lifetime ($\sim$55μsec) of uranyl ion that results in a low fluorescence pulse density in the measured signal.

The determination of uranium in natural waters by fluorescence methods at parts-per-billion (10^9) levels has been reported by several investigators.[1-6] Using conventional fluorescence techniques, Danielsson, et. al.[1] were able to determine uranium in water containing 7 ppb U or less. Their method used an ion exchange purification step that also concentrated the uranium to about 150 ppb in the measured solution. Karkisch[2,3] et.al., who also used ion exchange pre-treatment were able to measure uranium at about the same level in natural waters. The detection method employed the extremely difficult to automate technique using an alkali metal fluoride flux. Using X-ray fluorescence, Hathaway et. al.[4] determined uranium in ground water at about the same level of concentration. Neutron activation[5,6] has also been used successfully at the same or lower levels of uranium but requires the use of high neutron flux experimental reactor.

Recently Richardson, et. al.[7] have demonstrated the increased sensitivity of fluorimetric measurements by several orders of magnitude using laser excitation instead of conventional light sources. They were able to detect riboflavin at the sub-part-per-trillion ($<10^{12}$) level by laser induced fluorescence. Richardson and Ando[8] subsequently determined polycyclic aromatic hydrocarbons at the same levels by this technique.

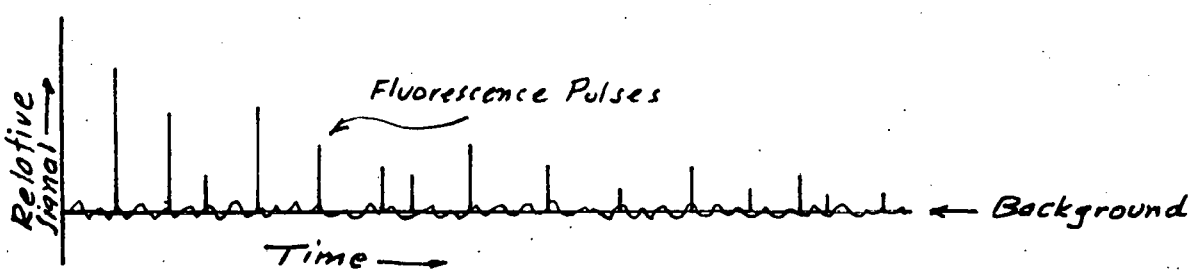
The objective of the work described in this paper was an attempt to extend the limits of detection of uranium by one or two orders of magnitude (<0.1 ppb) using the laser-induced fluorescence technique mentioned above.

Experimental

Because we decided to use the ion exchange pre-treatment method of Danielsson, et. al.[1] for purification and a twenty-fold concentration of uranium, a known solution containing 200 ppb U (corresponding to about 10 ppb

in a water sample) was prepared and used in the measurements. The electrolyte employed was 1.35 M in both H_2SO_4 and H_3PO_4. The instrumental setup (Fig. 1a) was the same as that used by Richardson and Ando[8]. A Molectron UV 1000 N_2 laser and a Molectron dye laser was operated at 30 Hz. The excitation wavelength was 305 nm (Rhodamine B, doubled) and the observed emission wavelength was 520 nm. An XP2020 PM tube was used as the detector at a maximum of 3000 V. A KV450 filter was placed in the light path just ahead of the PM tube.

Several measurements of the time-resolved fluorescence spectrum were obtained for the 200 ppb uranium solution and recorded after boxcar integration of the signal. Prior to boxcar integration the signal was sent through an integrating amplifier. A typical plot of the time-resolved fluorescence is shown in Fig. 2. It can be seen that an order of magnitude less uranium could probably be detected (1 ppb in a water sample) at the limit. This limit of detection does not present any advantage over that obtained by previous workers. The reason a lower limit of detection is not feasible in this case is that in using the boxcar integrater, the major portion of the signal being integrated is the near zero (on the average) background. The fluorescence pulses are present for only a small fraction of the total integration time. This is shown in the representation below:



Gating the photomultiplier tube and pre-integrating/amplifying the signal could improve the signal to background ratio.

Because of the above limitation, an attempt was made to count fluorescence pulses and discriminate against background by means of the circuit shown in Fig. 1b. In this scheme each laser pulse (30 Hz) triggers a signal source in order to provide a window pulse (100μs long) to the gate of a high frequency pulse generator operating at 2 MHz. This generator then provides a 100μs pulse-modulated signal that is fed to the START terminal of an ORTEC Model 457 time-to-pulse-height converter along with the PM tube signal at the stop terminal. Whenever a fluorescence pulse is preceded by one of the modulating pulses at the START input, its time from START is determined and the time of occurrence of each fluorescence pulse during the window is stored in the appropriate channel of an ORTEC spectrum analyzer.

Several time-resolved measurements of the same 200 ppb U solution were made. This measurement method resulted in the same degree of success in obtaining a lower detection capability as the boxcar integration method. For a typical 200 sec. run, the total counts of all channels in the window pulse was 25.9K for the 200 ppb U solution while the blank produced 6.5K counts.

Discussion

It became obvious during the experiments that a fundamental reason existed to prevent a significant improvement in obtaining a lower detection limit for uranium by observing its time-resolved fluorescence spectrum.

Initial measurements showed that the fluorescence lifetime of uranyl ion was about was about 55 μsec. The fluorescence lifetime of riboflavin for example, is on the order of 5 nsec; a difference of 4 orders of magnitude. As a result,

fluorescence photon energy for uranium is spread over time such that the fluorescence peak density is low. This low density negates the advantages of boxcar integration techniques for effective measurements of long lived fluorescent species.

The counting technique fails because of the same fundamental reason - not enough pulses per unit time. This could be overcome by counting the pulses for a greater number of time units in two ways; (1) increase the laser pulse rate by a factor of 300 (not possible with the Molectron). If this could be done the total counts would be about 26K x 300 in the same real time and the signal to noise ratio would improve by $(26 \times 10^3 \times 300)^{1/2}/(26 \times 10^3)^{1/2}$ or 17 times. (2) increase the total counting time at the laser pulse rate of 30 Hz to obtain the same total counts as above. This would require over 16 hours and is impractical.

It appears, therefore, that the determination of long-lived fluorescent species such as uranyl ion at the parts-per-trillion level is not feasible using the measurements methods described. Perhaps other approaches to the problem would be more fruitful.

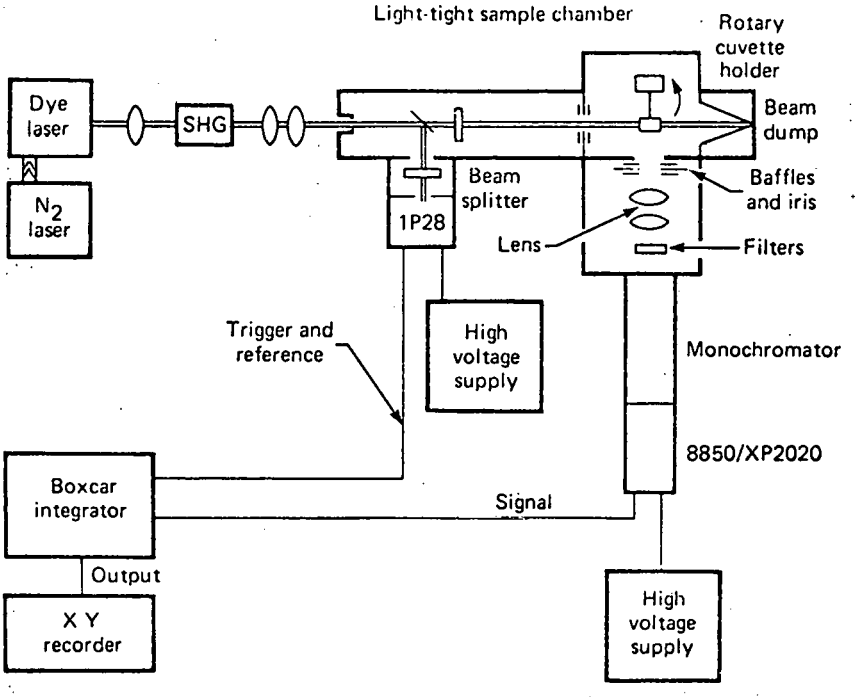


Figure 1a. Schematic of the experimental apparatus used

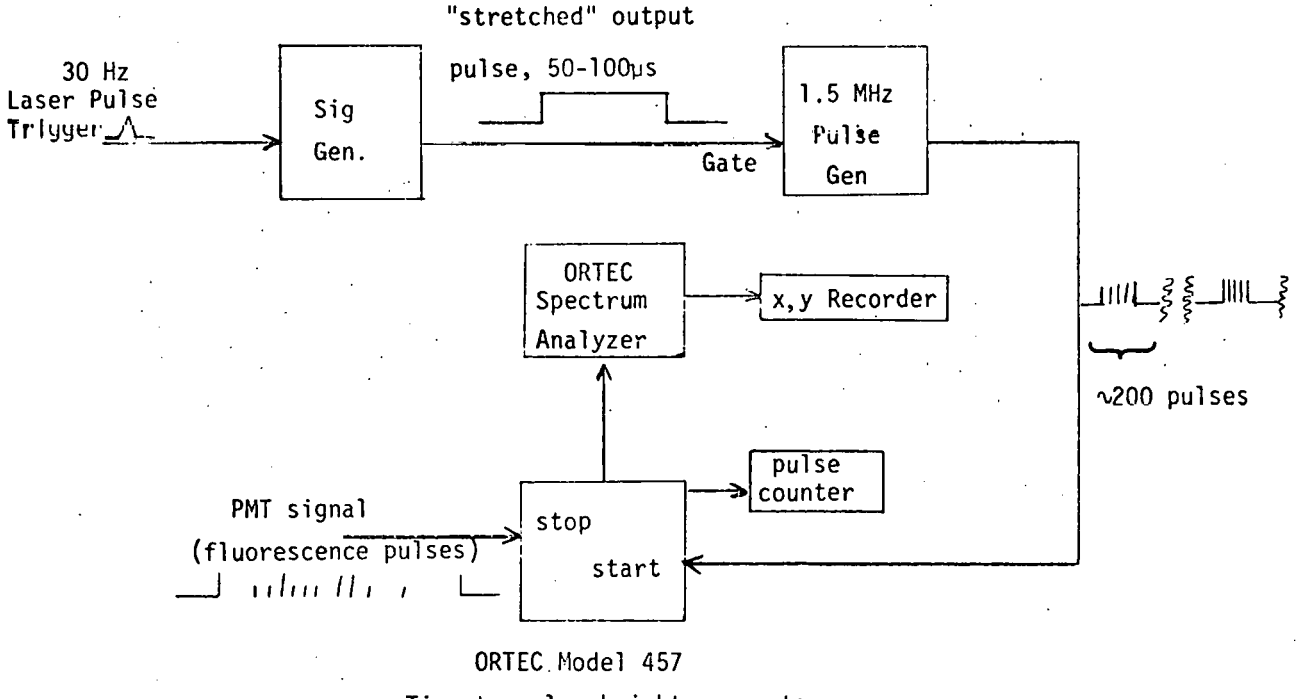
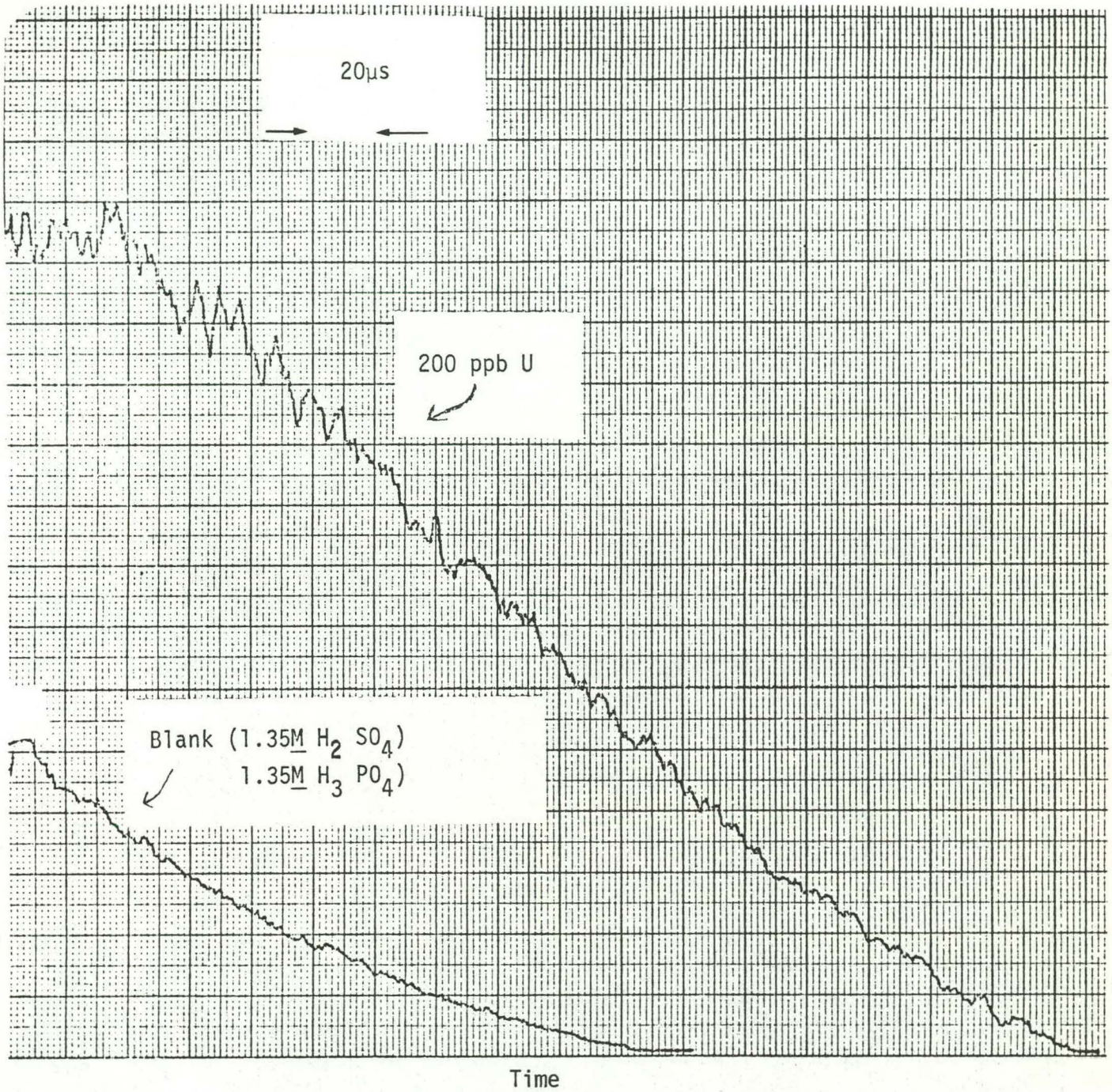


Figure 1b. Schematic of circuit used to count total pulses during 50-100μs window.



Figured 2. Time-resolved plot for uranium (200 ppb) in 1.35M H_2SO_4/1.35M H_3PO_4.

References:

1. Allan Danielsson, Bengt Rönnholm, Lars-Erik Kellström, and Folke Ingman, Talanta 20, 185 (1973).

2. J. Korkisch and H. Krivanec, Talanta 23, 295 (1976).

3. J. Korkisch and L. Gödl, Anal. Chim. Acta 71, 113 (1974).

4. Lawrence R. Hathaway and Gerard W. James, Anal. Chem., 47, 2035 (1975).

5. R.J.N. Brits and M.C.B. Smit, Anal. Chem., 49, 67, (1977).

6. Ernest S. Gladney, James W. Owens, and John W. Starner, Anal. Chem. 48, 973, (1976).

7. J. H. Richardson, B. W. Wallin, D. C. Johnson, and L. W. Hrubesh, Anal. Chim. Acta, 86, 236 (1976).

8. J. H. Richardson and M. E. Ando, Anal. Chem., 49, 955 (1977).

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