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# Historical Development and Potentiality of LED-fluorimeter

D.P.S. Rathore*

**_Abstract_**

*Pulsed LED-fluorimetry is a highly sensitive, versatile, and well-documented field technique for the direct determination of uranium in water samples at the* $\mu gL^{-1}$ *levels. Pulsed LED-fluorimetry has been utilized to assess uranium in a variety of matrices, including mineralized rocks, ores, beneficiation products, and other matrices, without the need for any kind of separation method. Using the high sensitivity of pulsed LED-fluorimetry, interferences from related and auxiliary elements are removed by a straightforward one-step dilution of the sample aliquots using push-button microliter pipettes, bringing the uranium concentration within the instrument's operating range. To improve the fluorescence, the measurement was carried out using the differential technique method, which uses a more appropriate acidic buffer mixture of* $H_3PO_4$*-*$NH_4H_2PO_4$ *(pH ~2.5, with* $H_3PO_4$ *at 1 M and* $NH_4H_2PO_4$ *at 2.17 M). In fact, it is the design of the entire experimental procedure in such a way that for very diluted sample solutions, the prefilter (species absorbing at the laser wavelength of 337 nm, LED wavelength of excitation at 400 nm) and postfilter (species absorbing at the maximum fluorescence wavelengths, 480-560 nm) effects are negligible (which is verified by spectrophotometry). The differential technique is a self-standardized methodology traceable to international standards. This paper describes the historical development and potentiality of versatile portable LED-Fluorimeter available in the market in the world as on today for reliable measurement of uranium in water, rocks, minerals, concentrates and other diverse matrices.*

**Keywords:** LED fluorimeter, development of instrumentation, uranium, water, rocks, minerals, concentrates, and diverse matrices

## INTRODUCTION

Due to its various features such as polyvalence (+4, +6), large atomic radius (0.97 Å), high chemical reactivity, relative solubility of U(VI) compounds in aqueous solutions, and relative insolubility of U(IV), uranium is found in many compounds. Many minerals contain uranium, which easily spreads and generates a wide variety of compounds. Hexavalent uranium was identified by the linear, polar uranyl ion $UO_2^{2+}$ (VI) under oxidizing conditions. The uranyl ions are very stable. Similar to many secondary uranium minerals, uranium ions preserve their identity through a variety of chemical changes. These secondary minerals are loosely held and cations may be added or removed by base exchange procedures without altering the $UO_2$ key layer. These are denoted by the generic compositions $A[(UO_2)(RO_4)]XH_2O$, $B[(UO_2)(RO_4)_2]XH_2O$, and $B\,[(UO_2)(CO_3)_2]XH_2O$ in the solids.

where A = K(I), Na(I), H(I); B = Ca(II), Ba(II), Mg(II), Cu(II), Fe(II), Pb(II); R = P(V), As(V), and

***Author for Correspondence**
D.P.S. Rathore
E-mail: dpsr2002@yahoo.com

Ex- Scientific Officer -G Atomic Minerals Directorate for Exploration and Research, Department of Atomic Energy, Jaipur, Rajasthan, India

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V(V). The solubility of these secondary uranium minerals in aqueous solutions varied. As a result, uranium can travel across a broad range of pH and Eh values in different uranyl complexes. Thus, in many surface or near-surface settings in natural water systems, uranium is a relatively mobile element [1–8].

The author including the Atomic Minerals Directorate was continuously involved in testing the performance and use of different instruments such as, UA-3 Uranium Analyzer (Scientrex, Canada) [4-8]; Laser–induced fluorimeter [4–8] and LED fluorimeter [4,5] developed by Raja Ramanna Centre for Advanced Technology(RRCAT), Department of Atomic Energy, Indore, India and later Quantalase Enterprises Pvt Limited, Indore, India.

This paper describes the historical development and potentiality of pulsed LED-Fluorimeter available in the market in the world as on today for reliable measurement of uranium in water, rocks, minerals, concentrates and other diverse matrices.

## DEVELOPMENT OF LASER-INDUCED FLUORIMETER:

One of the major programs at the Center for Advanced Technology (CAT), now known as the Raja Ramanna Center for Advanced Technology (RRCAT), is to develop technologies for various lasers and explore their applications in various fields, particularly those of the Department of Atomic Energy. As part of this program, we developed a nitrogen laser-based fluorimeter for the detection of uranium in water samples. Uranyl molecules strongly fluoresce upon excitation. This property of uranyl ions was used to develop an instrument for measuring the ultralow concentrations of uranium in water. Figures 1 and 2 show the excitation and emission spectra of uranyl species in water. The findings of a round-robin inter-laboratory study on the use of time-resolved emission spectroscopy for uranium (VI) speciation under aqueous conditions are noteworthy.

Based on these studies [9], (i) electronic excitation was localized within the $UO_2^{2+}$ group. (ii) A vibronic fine structure was observed in both the absorption and luminescence spectra depending on the nature and symmetry of the species. Emission spectrum analysis, rather than lifetime value analysis, can be used to determine the spectroscopic signatures of certain U(VI) species. (iii) A complete description of the medium (chemical composition and total ionic strength) is necessary to allow comparison of the lifetimes of free U(VI) and probable uranyl complexes.

Specific spectral signatures for the emission of the uranyl species were observed.

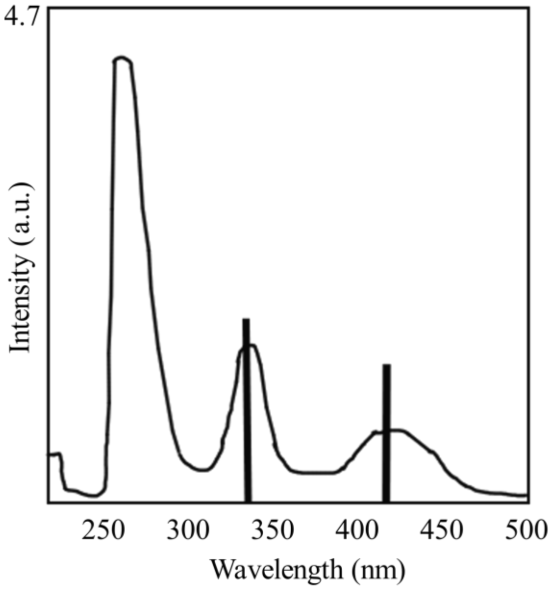

**Figure 1.** Excitation Spectrum of Uranyl.

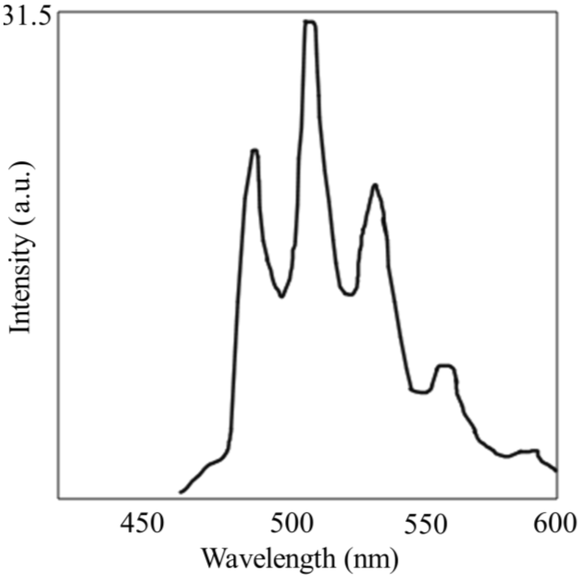

**Figure 2.** Fluorescence spectrum of uranyl.

**Figure 3.** Laser Flurimeter (Photograph Courtesy RRCAT).

The image displays the first apparatus developed by the Department of Atomic Energy's Centre for Advanced Technology in Indore, India, for measuring the content of uranium in water samples. This instrument used a pulsed Nitrogen laser emitting a pulse of light at 337 nm wavelength with pulse width of a few nanoseconds. This light excites uranyl molecules, which then emit fluorescence in the wavelength band 475–575 nm. The fluorescence spectrum of uranyl species is well characterized and documented in the literature, with a main fluorescence wavelength band of 475–575 nm [9–11]. A Photomultiplier Tube measured the intensity of this fluorescence, from which the concentration of uranium in the water.

The samples were then analyzed. One such instrument was also given to *the nuclear application* laboratories of IAEA in Seibersdorf, Austria (Figure 3).

Later, RRCAT developed a compact version of this instrument, the technology of which was transferred to Quantalase Enterprises Pvt., Ltd. The instrument manufactured by Quantalase is shown in (Figure 4).

**Figure 4.** Laser Fluorimeter (Quantalase).

The instrument has three modes of operation: standard, spiking, and counting. In Standard Mode, the instrument was first calibrated using a standard solution of uranium, and then measurements were performed on the samples. In Spiking Mode, fluorescence from the sample was measured, a known quantity of standard solution was added to the sample, and fluorescence was measured again. From these measurements and knowing the volume and concentration of the standard solution, the instrument calculated the concentration of uranium in the sample. The advantage of this mode is that it automatically compensates for any process that can reduce the fluorescence from the sample, such as impurities that quench the fluorescence, absorb it, or reduce the turbidity of the sample. Only fluorescence from the sample was measured in Count Mode [4]. Stable and repeatable instrumental responses were obtained. The examination of uranium only takes 1-2 minutes. The instrumental response varied at low laser intensities. An analysis using this instrument should be avoided if oscillations continue. The laser tube must be changed, as the instrument's instruction booklet suggests.

## DEVELOPMENT OF PULSED LED-FLUORIMETER

The Laser fluorimeter described above has a serious problem, namely, the very short life of the nitrogen laser tube. To overcome this problem, in 2006, Quantalase developed a fluorimeter that used an LED instead of a nitrogen laser to excite the fluorescence of uranyl in the samples. The nitrogen laser emitted at a wavelength of 337 nm, which is near the center of the middle peak of the uranyl excitation spectrum shown above. Unfortunately, LEDs that emit at this wavelength are not commercially available. Hence, we decided to use LEDs emitting at 400 nm, which is near the center of the third excitation peak.

There were several technical problems which were overcome and finally two years later the first model of the LED fluorimeter for measurement of uranium concentration in water was made available to users. This model is illustrated (Figure 5).

As a result of ongoing research and development, this fluorimeter underwent a number of changes, and soon after, the LED Fluorimeter Model LF2 (Figure 6) was introduced to the market.

A light-emitting diode (LED) produces 400 nm wavelength pulses with an average duration of 20 µs and an energy of 20 µJ. The LED pulses repeat at 1000 pps on average. The LED beam only allows UV light to pass through a strong cutoff UV filter. The cuvette containing the samples was exposed to UV light. The fluorescence of uranium in the sample falls on the photomultiplier tube because the long-pass filter prevents ultraviolet (UV) light from the LED.

**Figure 5.** LED fluorimeter (Quantalase).

**Figure 6.** LED fluorimeter Model LF2 (Quantalase, India).

After the LED light passed through the sample-containing cell, it was absorbed by using a beam dump. The LED light interfered with transmission in the absence of a sufficient beam dump.

Normally, the photomultiplier tube is maintained in an off state. The LED pulse is picked up by a detector that alerts the controller circuit. After an appropriate amount of time, the photomultiplier was turned on using a signal from the controller circuit to the power supply. The fluorescence of any organic molecule in the sample activated by the LED decayed to almost zero during this delay period. The instrument is highly repeatable owing to its appropriate pulse energy, delay configuration, and averaging across a large number of pulses. The technical features of the LED fluorimeter (Model LF-2) are listed in Table 1.

The most sensitive and adaptable portable device for uranium concentration measurements available at the time was this one, which can measure uranium concentrations as low as 50 parts per trillion (PPT) \http:// quantalase.in) [4]. More than 100 of these devices have been provided by

Quantalase to DAE laboratories, academic institutions, and businesses across India, and another automated version of this device, which is currently being developed, can simultaneously measure the uranium content in up to 16 samples.

**Table 1.** Technical specifications of LED fluorimeters, Model LF-2. The average of 1280 measurements was used to calculate the uranium concentration. Pulsed UV LEDs (Light Emitting Diodes) emitting at 400 nm wavelength and with a suitable filter. Twenty microjoules or higher, less than 1%, five years.

| Detector | Analyte volume | Dynamic range | Accuracy | Reproducibility | Averaging |
|---|---|---|---|---|---|
| Photomultiplier tube with precision multilayer optical filter. | 6ml cuvette Made from Ultra low fluorescence Fused Silica. | 0.1 – 1000 ppb (0.1 - 1000 microgram per litre). | Better than 10%. Can be significantly better if the instrument is used in temperature controlled environment. | Better than 5 % | The average of 1280 measurements was used to calculate the uranium concentration. |

*LED Fluorimeter: Quantalase Enterprises Private Limited, Indore,India. (http://quantalase.in)*

## DIFFICULTIES IN RELIABLE URANIUM ANALYSIS IN NATURAL WATERS

Because it might be difficult to preserve natural water samples, water analysis is much more complex owing to the wide range of water samples that vary in their amounts of total dissolved salts, including saline water and fluoride content [12–22]. We discovered that, as extensively covered in the most recent review [22], the time gap between sample collection and analysis is the most important component responsible for reliable analysis of water samples, particularly in hot, arid environments.

## URANIUM MEASUREMENT IN MINERALS, ROCKS, AND OTHER DIVERSE MATRICES

Balaram and Sawant [5] recently examined the portable analytical tools available for use in mineral exploration studies. With the advent of bright and stabilized LED lights, a pulsed LED fluorimeter based on this excitation source has become available from Quantalase Enterprises Pvt. Ltd. (Indore, India).

In comparison to water samples, mineralized rock sample solutions are easy to analyse using the application of the differential technique of laser-induced fluorimetry/pulsed LED-fluorimetry for their uranium content due to their easy preservation over a period. Laser-induced fluorimetry/pulsed LED-fluorimetry is a well-documented, highly sensitive and versatile technique for the determination of uranium in water samples at $\mu g\ L^{-1}$ levels [5–8, 24].

The research group of Atomic Minerals Directorate and others has utilized the potentiality of the application of differential techniques in laser/LED-fluorimetry for the determination of uranium in rocks, minerals, concentrates, and other diverse matrices and has been well-documented [23]. The tolerance levels of numerous related interfering elements were improved by nearly ten times in this novel LED-based approach, which uses LEDs in the visible range (400 nm) to replace UV lasers (337 nm). It has been discovered that pre-filters such as Fe(III) can be tolerated well (10 fold increase as compared to laser-induced fluorimetry). Post-filters such as Mn, Cu, and Cr work in the same way. There has been at least a ten-fold increase in tolerance to numerous ions when comparing LED fluorimetry to laser-induced fluorimetry [24].

The use of a differential approach in pulsed LED fluorimetry and laser-induced fluorimetry has strong meteorological qualities by nature. The following fundamental requirements are satisfied by the use of different techniques in laser/LED fluorimetry: high precision and accuracy; applicability to a range of sample matrices for a broad spectrum of applications throughout the nuclear fuel cycle; and simplicity, efficiency, and ease of use, including equipment calibration, method standardization and operation, equipment calibration, economic viability, eco-friendliness, high sample throughput, comparability, and traceability. A self-standardized measuring methodology, the differential technique, ensures the accuracy of the analytical results [25].

A pulsed LED-fluorimeter (Figure 6) is a great replacement for the UA-3 laser-induced fluorimeter (Scientrex, Canada) that is currently on the global market for uranium determination in various matrices in the nuclear fuel cycle, including hydrogeochemical reconnaissance surveys for field and base laboratory investigations (Figure 7).

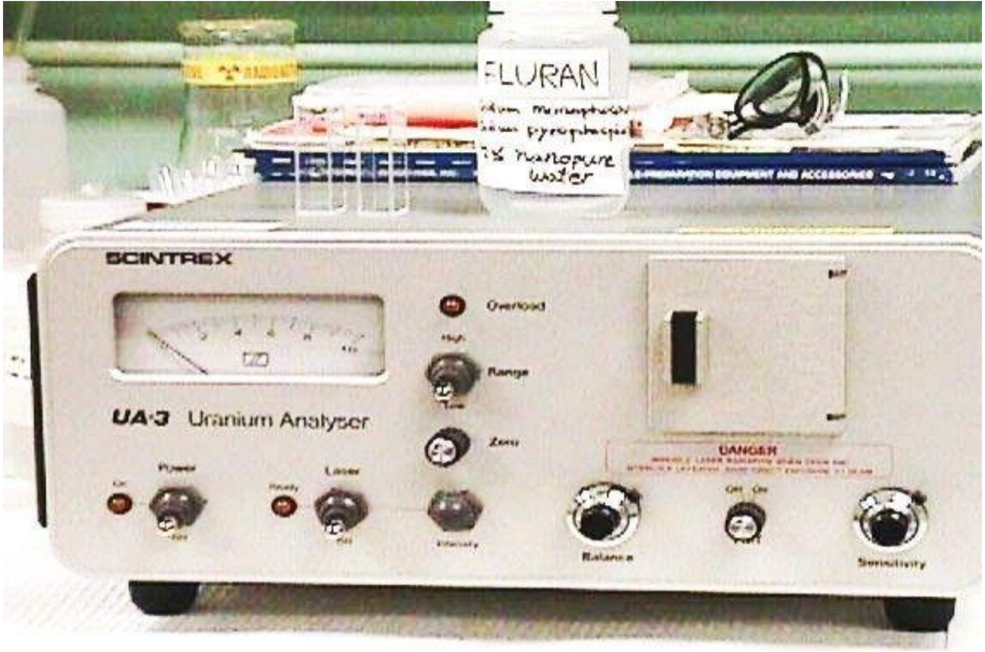

**Figure 7.** UA-3 Uranium analyzer (SCINTREX, Canada).

## CONCLUSIONS

With its simple equipment calibration and standardization, high sensitivity, improved reproducibility, affordability, environmental friendliness, traceability, and comparability in water, rocks, minerals, and other diverse matrices throughout the nuclear fuel cycle, LED-fluorimetry is a portable device that is more suited for accurate measurement of uranium for their sustainable growth globally.

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