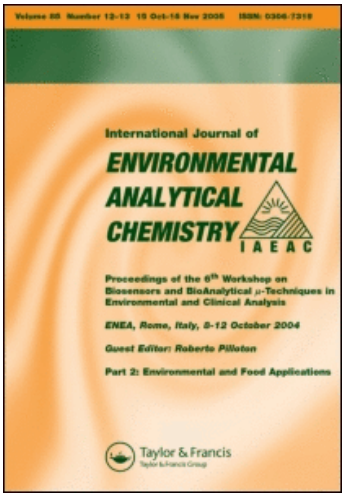

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Trace Determination of Uranyl Ion Using a Blue Led as Excitation Source in Phase-Resolved Luminescence Spectroscopy

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TRACE DETERMINATION OF URANYL ION USING A BLUE LED AS EXCITATION SOURCE IN PHASE-RESOLVED LUMINESCENCE SPECTROSCOPY

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A phase-resolved luminescence system based on the use of a light emitting diode (LED) is applied to the trace determination of uranyl ion (UO_2^{2+}). The system performance is evaluated, phase resolved spectra of $UO_2^{2+}$are shown as well as its lifetime determination using multifrequency phase resolved measurements. Analytical figures of merit are also presented for this system. A limit of detection (LOD) of 10 μg/L is obtained at the blue LED excitation wavelength of 460 nm and its results compare well with a conventional system. Also, a linear dynamic range of ca. 5 orders of magnitude is observed. In situ quenching correction of the analytical signal was evaluated and was applied to a real sample for uranyl determination.

Keywords: Blue LED; uranium; luminescence; frequency domain

INTRODUCTION

Current research in uranium chemistry is motivated by fundamental and applied scientific interest as well as practical demand. In this sense the need for a sensitive, fast, and accurate method for the determination is particularly felt in the environmental, geological, and bioassay fields[1–3].

The photoluminescence emission of the uranyl ion (UO_2^{2+}) has long been used for the determination of trace quantities of uranium[4–7], where the conventional fluorometric method of uranium analysis consists of obtaining a pellet from the

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uranium sample by fusion with sodium fluoride in a platinum crucible[8,9] and later on the time resolved laser induced fluorescence (TRLIF) has been proposed to the trace determination of uranyl ion[5,7]. The latter technique has been proved to be, by far, the most sensitive with detection limits ranging from 0.001 to 1 μg/L typically.[5,7]

Within the luminescence spectroscopy techniques, in the last years there has been a great advance in the use of Phase Resolved Luminescence Technique (PRLT), caused mainly from the need in areas like biochemistry, chemical kinetics and analytical chemistry[10,11]. Some advantages of the PRLT lie in their accuracy, quickness and in a somewhat simpler instrumentation than their equivalent time resolved techniques. The two major factors that limit the precision and accuracy of quantitative photoluminiscence measurements of UO_2^{2+} in real samples are the fluorescence from organic compounds in the samples and the species present in the real sample that can quench the excited state of the uranyl ion ($^*UO_2^{2+}$) through several possible non-radiative paths. These problems can be solved by measuring simultaneously the intensity and the lifetime of the luminescence signals, that promise the in-situ quenching correction of luminescence signals. Moreover, phase shift luminescence signals can be varied by allowing to change the frequency, then permitting stray light rejection like the fluorescence of the organic compounds and improvement of selectivity. Usually, phase shift and demodulation of the emission signal are measured using either continuous laser (cw) or a Xe arc lamp as excitation source where modulation is achieved using either acoustooptical or electrooptical devices by either fixed or variable frequency drivers.[12,13] More recently, solid state light-emitting devices, such as light-emitting diodes (LEDs), have been used as excitation sources in PRLT[14,15] as well as in time resolved spectroscopy.[16]

The recent advances in communication technology have encouraged the development of LEDs having more power emission and with shorter emission wavelengths. The use of LEDs as light excitation source for luminescence has become a real possibility, they are stable, small and easy to modulate at frequencies up to above megahertz. Besides, they have a low divergence angle which permits their direct use. Among the disadvantages of LEDs are their low output power and limited wavelengths of emission.

In this paper the feasibility of trace determination of uranyl ion using a Blue LED as excitation source in luminescence spectroscopy in the frequency domain is demonstrated. The determination of uranyl ion in a real sample with the implementation of a fast, simple and accurate methodology for signal quenching correction is shown.

THEORY

The phase fluorometer theory has been discussed in detail by some authors[10,11]. For a single exponential decay system, it has been shown that when the luminescent species is excited by modulated light at frequency (ω), the lifetime (τ) can be calculated either from the phase shift:

$$tan(\phi) = \omega\tau = 2\pi f\tau \tag{1}$$

where f is the linear frequency or from the demodulation factor

$$m = cos(\phi) = [1 + (2\pi f\tau)^2)]^{-1/2} \tag{2}$$

Straight phase shift of the signal can be measured directly with a dual channel lock-in amplifier (LI). The output of the two-phase sensitive detectors are denoted by the in-phase (P) and in-quadrature (Q) components of the signal.

Total signal (S) can be obtained by

$$S = (P^2 + Q^2)^{1/2} \tag{3}$$

and the phase shift (ϕ) with respect to a reference, can be calculated from

$$\phi = tan^{-1}\,(Q/P) \tag{4}$$

Assuming that all the light detected corresponds to the emission of the species having a lifetime τ, from 1 and 4 we have:

$$2\pi f\tau = Q_\tau/P_\tau \tag{5}$$

where an explicit dependence of P_τ and Q_τ with τ can be immediately recognized. As scattered light is present in most of the measurements, the measured signal is composed by the scatter and the emission signal. It is reasonable to assume that the scattered light is in phase with the reference (or the excitation beam) then, the in-phase component can be broken down as:

$$P = P_S + P_\tau \tag{6}$$

where P_S and P_τ represent the contributions of scattered light and the in-phase component of the luminescence while Q_τ, which remains unaffected, can be simply called Q.

Solving P_τ from eq. 5 and using eq. 6, we obtain:

$$P = P_S + (2\pi\tau)^{-1}\,Q/f \tag{7}$$

This expression leads to $(2\pi\tau)^{-1}$ as the slope of the plot of the in-phase component vs. Q/f for several frequencies. The lifetime of the excited species can be obtained, even in the presence of scatter, by measuring the Q and P components of the signal at different frequencies.

EXPERIMENTAL

LED – Specifications

A commercially available blue LED was employed (Nichia Chemical Industries, Japan, Model NSPB 500) having the following specifications: main wavelength 470 nm, bandwidth 20 nm, luminescence output 3 mW at polarization current (I_p) of 20 mA and a recommended maximum I_p of 30 mA. To control I_p an 11 Ω resistance was placed in series with the LED. As the emission intensity is function of the polarization current, a sinusoidal signal from a function generator with an output impedance of 50 Ω was applied to modulate it. I_p was fixed with the potential applied (typically at 9 V DC and 12 $V_{p\text{-}p}$,) so that the LED remained on along a cycle.

Luminescence measurements

Luminescence measurements were carried out using three different systems: 1) a LED excited phase resolved system; 2) a conventional DC spectrofluorometer and 3) a Laser based time resolved system.

SYSTEM 1

The experimental set up is shown in Figure 1 and the main components and specifications of the system are listed in Table I. The cell holder was designed to accommodate a 5-faces optical fluorescence cuvette with a 1 cm optic pathway. Two different excitation geometries were tested:

System 1.A

The blue LED is placed at the bottom of the cell holder without focusing optics in such a way to produce a narrow cone which mimics the actual geometry of the entrance slit of the monochromator. This was a simple and compact arrangement and yielded the maximum amount of light collected.

System 1.B

The blue LED illuminates one side of the cuvette after passing through the two quartz lenses (2.5 cm diameter, 4.6 cm and 2.4 cm focal distance). The exciting

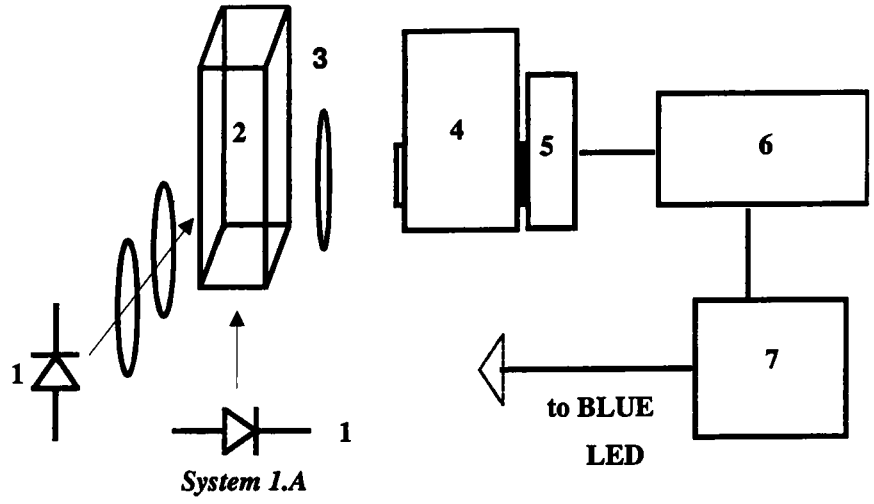

FIGURE 1 Experimental Set up: 1.- Blue LED (according to two different geometries *system 1.A* and *system 1.B*; see text), 2.- Fluorescence cell, 3.- Lenses, 4.- Monochromator, 5.- Photomultiplier tube, 6.- Lock-in Amplifier, 7.- Function Generator

light path goes at 90° with respect to the entrance slit of the monochromator. This particular arrangement allows a better control of the scattered light, but also shows a smaller sampling volume to collect the light.

TABLE I Equipment and experimental conditions employed in the System 1

Component	*Model*	*Conditions*	*Manufacturer*
LED	NSPB-500	R_L= 11 Ω, V_{AC}=10–12 V, V_{DC}=9 V	Nichia
Monochromator	77200	Diffraction grating = 1200 lines/mm. Slit width = 9 nm	ORIEL
Photomultiplier	R928	H.V.= 900 V	Hamamatsu
Lock-in Amplifier	SR850	Time constant 1 s.,	Stanford Research
Function Generator	3310B	Variable frequency	Systems Hewlett Packard

Procedure for lifetime determination

The reference signal for the lock-in was supplied with the TTL output of the function generator employed to polarize the LED.

To determine the emission lifetimes of uranyl ion, the phase shifting technique described above was used. Reference phase shift from a "zero-lifetime" emitter was accomplished by placing in the cell holder a cuvette with aqueous solution of a laser dye colorant (LD490). Lifetimes were obtained with the procedure given above (measuring, as already explained, the Q and P components at several frequencies). The reference phase shift was corrected.

SYSTEM 2

A conventional spectrofluorometer (Farrand, Mark I) was used to measure luminescence intensities. A time constant equivalent to 1 s was selected in the damping control. Excitation wavelength was 420 nm and emission wavelength was chosen at 517 nm with a 20 nm bandwidth.

SYSTEM 3

The TRLIF technique has been previously described[17]. Briefly, it consists of a N_2 laser (2 mJ output energy at 337 nm, 10 ns pulse) as the excitation source. The luminescence signal was collected at 90 degrees after passing through a 10 cm monochromator (ORIEL) joined with a Hamamatsu R928 PMT. The signals were digitized and stored with a LeCroy model LSD −140 and subsequently processed in a PC.

Materials

Stock solutions were prepared by directly dissolving solid $UO_2(NO_3)_2.6H_2O$ (Merck) and used without previous treatment. Subsequent dilutions were made 1 M in H_3PO_4. Aqueous solutions were prepared with distilled, deionized water. Chloride solutions for quenching correction evaluation were prepared dissolving NaCl (Merck) concentrate and added up to the uranyl solutions.

Real sample

A selected portion (ca. 500 g) from a uranium claim (Maria Rosa, Córdoba, Argentina) was sampled. After drying and grinding properly, samples were processed using a known procedure[5]. Final solution was made up 1 M in H_3PO_4.

RESULTS AND DISCUSSION

Luminescence of uranyl ion

In Figure 2 is shown the uranyl emission intensity as a function of the excitation frequency for the in-phase (P), quadrature (Q) and total signal (S). The Q component presents a maximum at $f=(2\pi\tau)^{-1}$ and decreases to almost zero at high and low modulation frequencies. On the other hand, the total and in-phase signal decreases steadily with frequency due to the demodulation factor. Therefore, it can be argued that there is a loss in the signal, by increasing the frequency. In fact, Figure 2 shows that the quadrature component recovers only *ca.* 50 % of the total signal obtained at low frequency in the best case. Nevertheless, measuring the in-quadrature signal permits to reduce the background signal level when scattered light is present.

In Figure 3 is shown the S and Q component of a phase resolved spectrum of the uranyl emission. It can be observed that the Q signal is free of scattered light produced mainly by the blue LED emission at a maximum of 460 nm. The latter signal can be considered like an emitter with zero lifetime and therefore all their contribution is over the P component and is readily seen when total signal is considered. The contribution of the scattered light was more important when *System 1.A* was used.

Determination of the emission lifetimes

In these experiments the *System 1.A* and an excitation filter were used. Even when this combination assured maximum light collection efficiency, scattering should be considered and therefore no direct phase angle measurement can be used to obtain luminescence lifetimes. As a matter of fact it represents the worse case for scattering interference and was used to test the system for lifetime comparison. Measurements were carried out with UO_2^{2+} solutions (10 mg/L in H_3PO_4 1 M). The in-phase component was plotted against Q/f at different frequencies to obtain emission lifetimes and the resulting plot is shown in Figure 4. A lifetime of (192.2 ± 0.5) μs was obtained in excellent agreement with the value of (192 ± 2) μs found when system 3 (TRLT) was used.

Linearity and detection limit for the uranyl detection

A log-log plot of the S and Q signals as a function of uranyl concentration is shown in Figure 5. Good linearity comprising five orders of magnitude is observed for Q. A somewhat poorer linear dynamic range is obtained for S (four decades). This difference can be accounted for the scattered light produced by

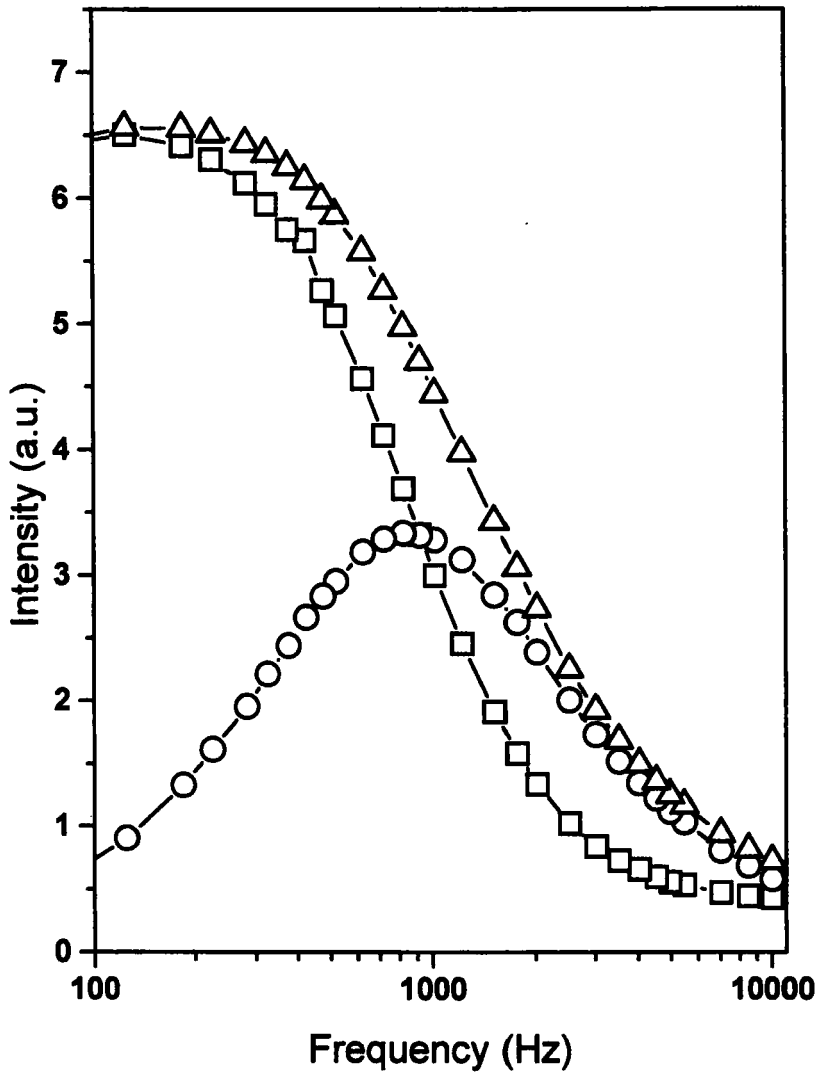

FIGURE 2 Components of the signal for the emission of the UO_2^{2+} (10 mg/L) as a function of the modulation frequency (f). P = -□-, Q = -O- and S = -Δ-

the excitation signal, whose contribution becomes progressively more relevant as the U(VI) concentration decreases.

Detection limits (LOD) at 975 Hz of modulation frequency for uranyl solutions in 1 M H_3PO_4 were obtained and are shown in Table II (minimum detectable sig-

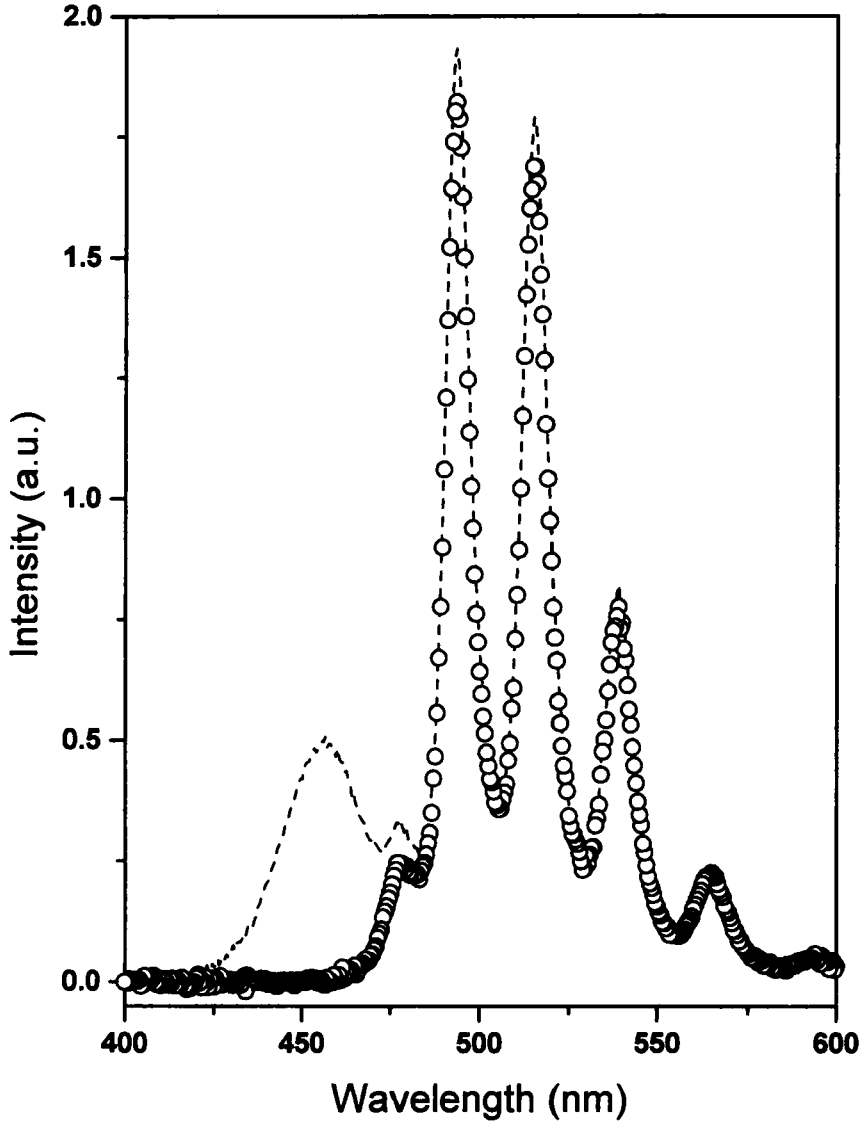

FIGURE 3 Emission spectra of UO_2^{2+} (1 mM in 1M H_3PO_4) solution at 2.5 KHz modulation frequency. Total signal S(---). Quadrature component (-O-)

nal was calculated as three times the standard deviation corresponding to the blank solution)[18]. The lowest LOD corresponds to the quadrature signal of the *System 1.A*; in this case there is a much more efficient light collection while *Q*

assures very efficient stray light rejection of the signal. Thus, very good S/N is achieved as compared when using total signals. This LOD was improved by adding a pass-band filter, placed between the LED and the bottom of the cuvette, which absorbs above 500 nm. In this case a LOD of 10 μg/L was obtained.

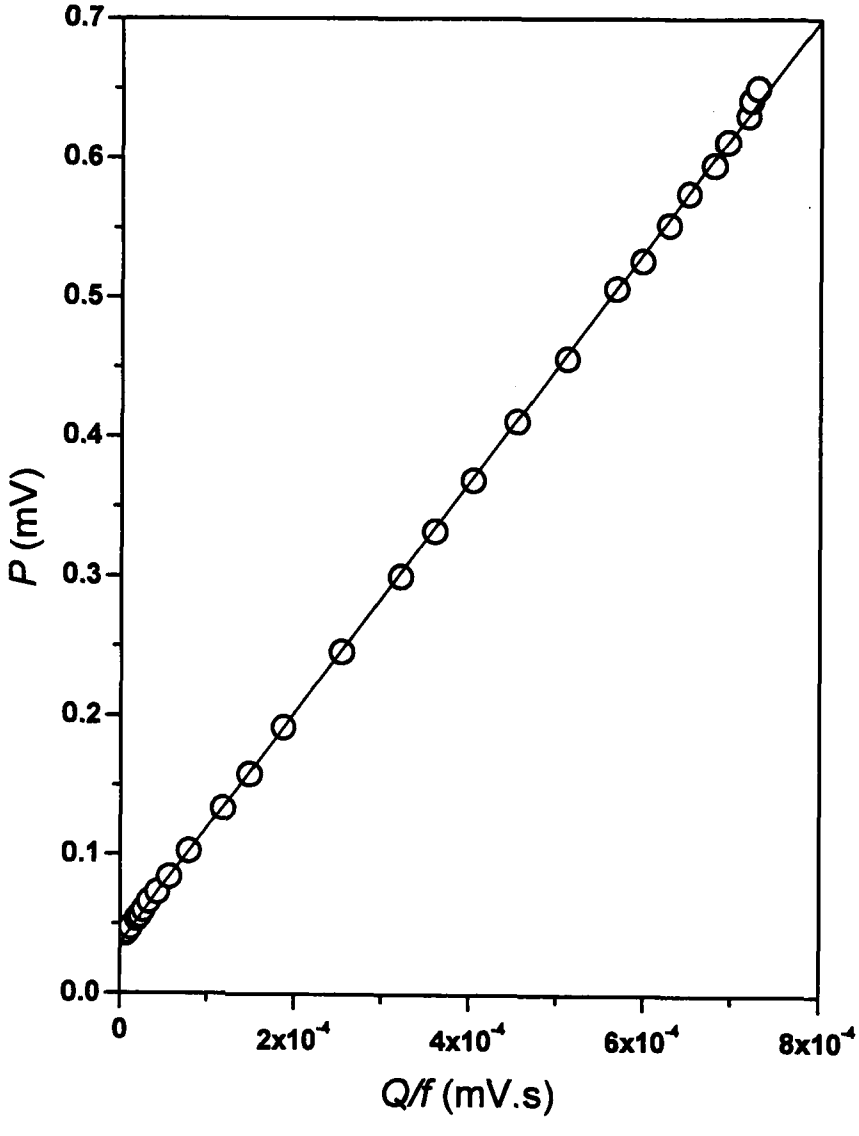

FIGURE 4 UO_2^{2+} emission lifetime determination using $P = P_S + (2\,\pi\,f\,t)^{-1}\,Q/f$. From the slope was obtained a lifetime of (192.2 ± 0.5) μs

TABLE II LOD (μg/L) for U(VI) in 1M H_3PO_4 at 975 kHz of excitation frequency for the experimental set-up

System 1.A			*System 1.B*		
P	*Q*	*S*	*P*	*Q*	*S*
77	26	50	101	74	49

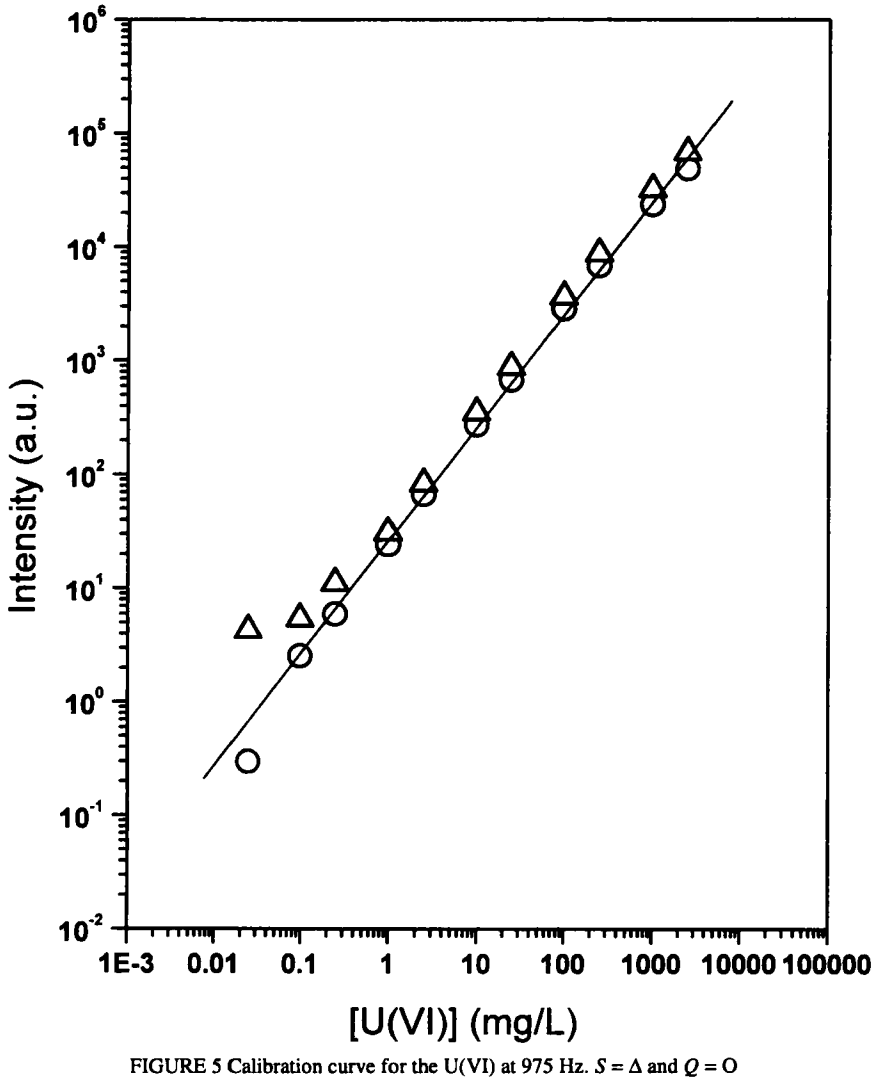

FIGURE 5 Calibration curve for the U(VI) at 975 Hz. $S = \Delta$ and $Q = O$

Using the *System 1.B*, appropriate focusing of the excitation light makes the whole arrangement less prone to the scatter light plague. Then, total signal is observed to have the best LOD for this arrangement. In Figure 6 is shown a graph of LOD vs *f*. It can be observed that the best LOD is obtained at a lower frequency, that is, when the intensity of the luminescence of the uranyl ion has a maximum. It should be stressed that the advantage of measuring Q component should be enhanced at low uranyl concentration in real samples where complexity added up by solution concomitants and scatter becomes more important.

By using a commercial spectrofluorometer and exciting in the maximum of the absorption band in which the blue LED produces the excitation of the uranyl ion (system 2), a 9 ppb LOD was found. Although the LEDs do not have the same emission intensity as other conventional sources, light modulation improves the S/N ratio, thus comparable and even better LODs were obtained by using the system described (Table III). It should be stressed that this system cannot compete with laser induced flurescence systems in sensitivity as clearly shown in Table III where limits of detection in the order of ng/L are obtained by using relatively inexpensive N_2 laser systems. Indeed, the fact that UV light also induces undesirable organic molecules fluorescence can be easily overcome by gated detection.[5–7] The practical realization of solid state, high duty cycle, blue diode lasers would give rise to a new approach for the determination and would greatly improve its LODs.

TABLE III LOD obtained using fluorescence methods

Method	*Chemical enhancer*	*Detection limit (μg/L)*	*Reference*
LED excitation (phase resolved, 975 Hz). *System 1.A.*	H_3PO_4 1M	10	This work
LED induced fluorescence	H_3PO_4 1M	2	This work
(25 Hz). System 1.A.			
Steady State (Farrand)	H_3PO_4	9	This work
Spectrofluorometry	H_3PO_4	40	[1]
Xe lamp induced fluorescence	Fluran	2.0	[1]
LIF	Fluran	0.05	[1]
Gated detection after laser excitation	Phosphate solution	0.001	[5]
	0.1 M + HNO_3		
	1M		
Gated detection after laser excitation	Fluran	0.001	[7]

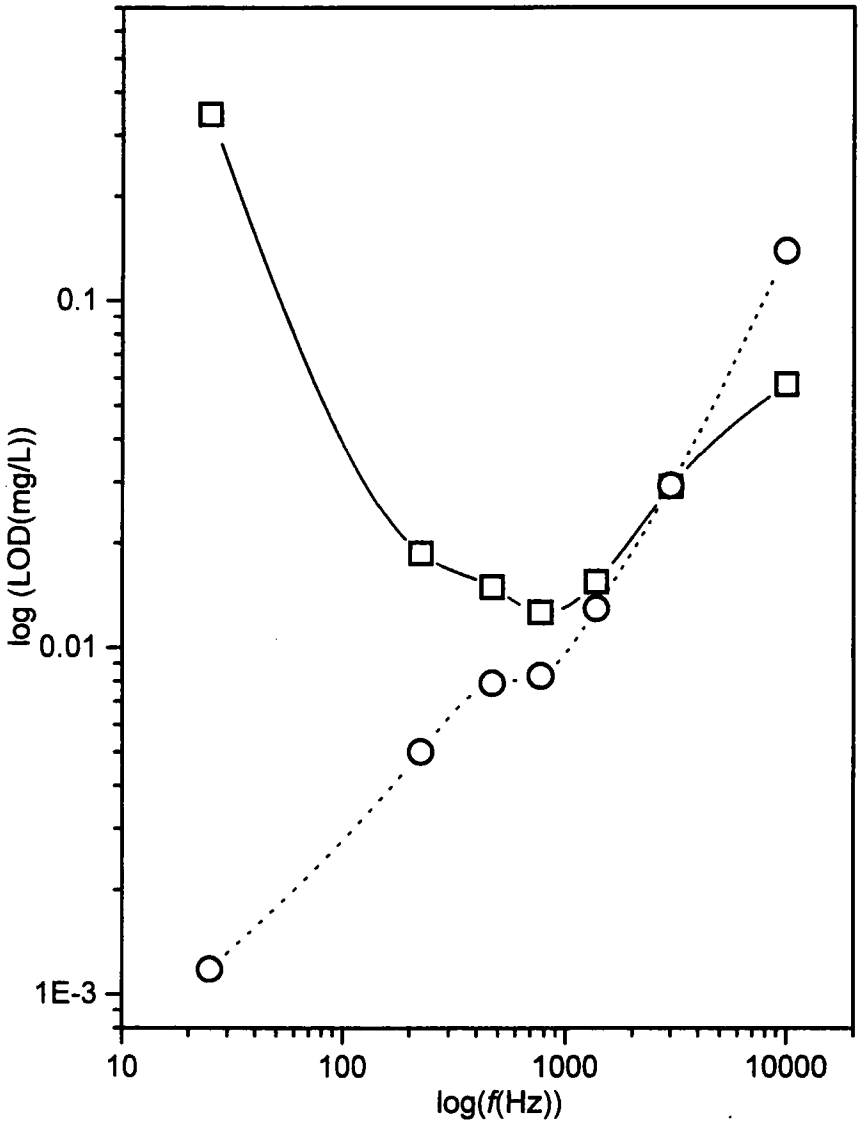

FIGURE 6 Limit of detection for the U(VI) at several frequencies for system 1.B. O – Total signal. □ – Signal in quadrature

Quenching effects correction

Quenching correction is important in real sample analysis. The problem with quenching arises when relatively long radiative lifetimes are involved, then

quenchers reduce lifetimes and subsequently lower the quantum yields. Quenching effects have to be accounted to avoid erroneous results when analyte sample content is determined against standard calibration curves[19].

Quenched corrected signals can be obtained by using intensity and lifetime measurements. The observed modulated emission signal is given by:

$$S = S_0[(\tau_0/\tau)^2 + (2\pi f\tau_0)^2]^{-1/2} \quad (8)$$

or

$$S = S_{0f}\{(1 + (2\pi f\tau_0)^2)/[(\tau_0/\tau)^2 + (2pf\tau_0)^2]\}^{1/2} \quad (9)$$

where S_0 is the modulated amplitude for an unquenched sample at very low frequency and S_{0f} is the unquenched signal at f. At very low frequency ($2\pi f\tau_0 \ll 1$) the demodulation attenuation is negligible; then S is directly measured at 25 Hz and the lifetime obtained from the procedure given above (eq. 7). Therefore, the unquenched modulated intensity at zero modulation frequency, S_0, can be calculated (eq. 6).

The *System 1.B* was used to measure both, total signal and lifetime measurement at different added [Cl^-] concentrations in the quenching reaction of $^*UO_2^{2+}$ by [Cl^-]. Recovered S_0 and unrecovered S signal were plotted against quncher concentration and are shown in Figure 7. It can be seen that even when almost one order of magnitude of signal is lost at higher quencher concentrations, good signal recovering is obtained. As no noticeable trend was observed, the recovered signal could be averaged giving a coefficient of variation of 2%. This is indeed a good value for quenching correction.

Quenching correction can be done with exactly the same set-up used in actual intensity measurement of standards and little time is involved in lifetime determination of the unquenched sample and the samples.

Uranium determination in a real matrix

Two replicates were processed as described before and lifetime measurements were made on both and also on the standard solutions prepared for the calibration curve. On the other hand, sample lifetimes were found, as expected, to be smaller than the standards. Quenching in sample solutions appears to be governed by the presence of concomitants present in the sample matrix. In fact, Fe^{3+} concentration in processed samples was determined by Flame Atomic Absorption Spectroscopy (FAAS) and an average value of 600 mg/L was found. Lifetime of uranyl was calculated considering the presence of Fe^{3+} and literature quenching rate constant[20], giving a value of 32 μs. This value agrees reasonably well with the experimental value. Fluorescence intensity measurements for calibration

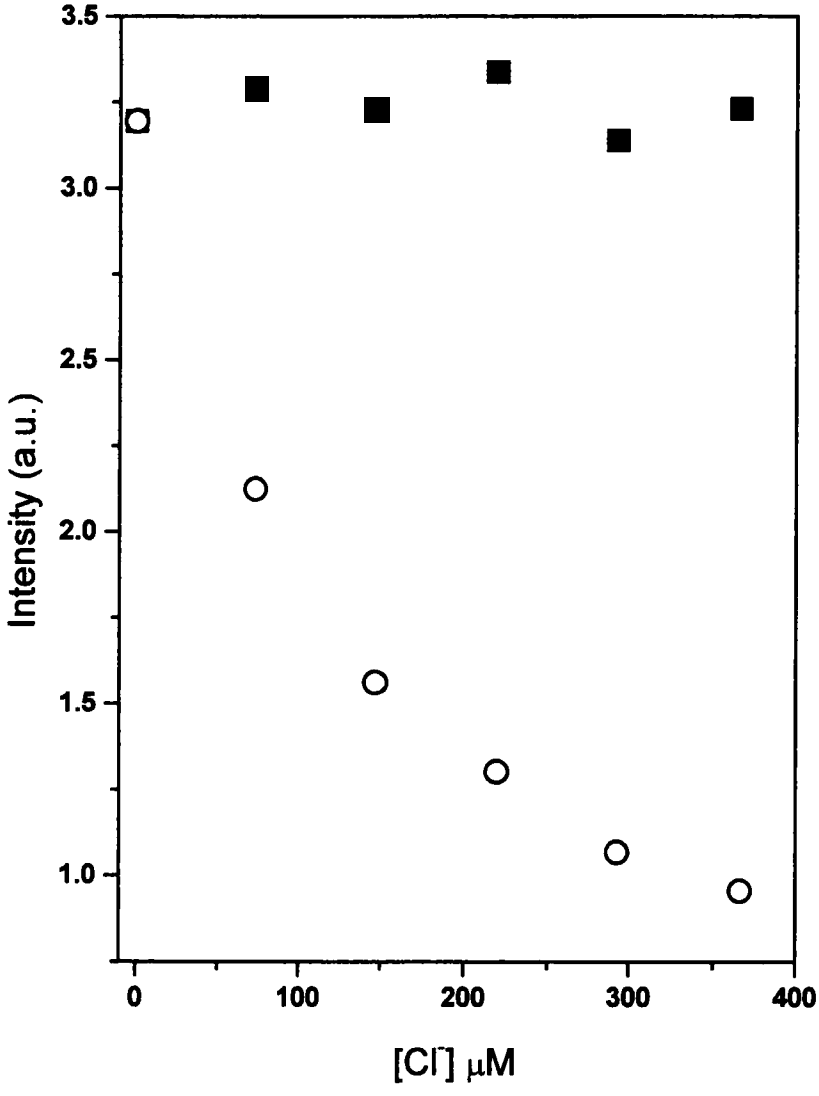

FIGURE 7 Intensity emission of U(VI) vs. the concentration of Cl^- ion. S, the observed modulated emission (O) and S_0 the modulated amplitude for the signal free of dynamic quenching (■)

curve and samples were carried out at 975 Hz and the resulting sample signals were quenching corrected (using eq. 9) in order to obtain the actual uranium values directly by interpolation from the calibration curve. In order to assess the reliability of these results, uranyl in processed samples was also measured by the standard addition method.

The principal figures of the calibration plot and the standard addition method are shown in Table IV and the corresponding results for the two replicates by using either technique. A good agreement is found. This implies that the quenching correction permits to make reliable determination of uranyl in a relative complex sample by using a standard calibration plot.

TABLE IV U content in the real samples

		Sample 1	*Sample 2*
Lifetime (μs)		(30 ± 3)	(30 ± 1)
Standard addition	slope.	(3.06 ± 0.05)	(3.35 ± 0.15)
	corr. coef.	0.99923	0.9995
	[U] (mg/L)	(49 ± 2)	(43 ± 5)
	U found in soil (%P/P)	(0.23 ± 0.01)	(0.20 ± 0.02)
Quenched corrected	[U] (mg/L)	(48 ± 2)	(51 ± 3)
signal	U found in soil (%P/P)	(0.23 ± 0.01)	(0.24 ± 0.01)

CONCLUSION

A simple and inexpensive luminescence system based on a blue LED excitation source has been successfully tested. Good LOD was obtained as compared with conventional fluorescence system, although well below laser induced systems, and excellent ability for lifetime measurements was demonstrated. Scattering of radiation precludes direct lifetime measurements through single dephase angle measurements so real time quenching correction is impaired. Nevertheless, this can be accomplished by multifrequency measurements with little expense of time. Quenching correction of samples luminescence can be carried out with the same set up, thus avoiding separation or standard addition methodologies.

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