

# Device for luminescence lifetime measurements of europium (III) ion based on a nitrogen-dye laser system

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An experimental system for measurement of luminescence lifetimes of lanthanide ions has been developed. It consists of a nitrogen laser pumped dye laser as an excitation source and two different kinds of registration devices based on boxcar integrator and transient recorder. Accuracies of both registration methods have been compared using the statistics of the measured data. The operation of the system in milli- and microsecond ranges has been verified using Eu(III) ions in H<sub>2</sub>O and D<sub>2</sub>O solutions.

## 1. Introduction

The trivalent lanthanide ions in their salts and doped crystals show sharp line fluorescence originating within the 4*f* when optically excited. In aqueous solution, fluorescence only from the middle part of the lanthanide series (Sm, Eu, Gd, Tb and Dy) is observed [1]. Following excitation, Ln(III) ions relax to sublevels of the ground electronic states.

Eu(III) and Tb(III) ions and chelates have been most extensively studied and used in practical applications [2], [3]. In aqueous solution, the dominant mode of luminescence quenching of these excited ions appears via coupling of the electronic excitation to O-H vibrations of water molecules in the inner-coordination sphere of Ln(III) ion. If deexcitation by coupling with another ligand is negligible, the rate of quenching is proportional to the number of OH bonds present in the primary coordination sphere of the cation [4], [5].

The reciprocal of the excited-state lifetime (the exponential decay constant,  $k = \tau^{-1}$ ) is the sum of individual rate constants of all the deexcitation processes. In aqueous solution, it can be expressed as

$$k_{\text{obs}} = k_F + k_{\text{nr}} + k_{\text{H}_2\text{O}} \quad (1)$$

where:  $k_F$  is the rate constant of radiative transition ( ${}^5D_0 \rightarrow {}^7F_j$ ),  $k_{\text{H}_2\text{O}}$  is the rate constant of nonradiative energy transfer to the O-H oscillators in the inner-coordination sphere, and  $k_{\text{nr}}$  represents the rate constants of non-radiative energy loss by all other pathways.

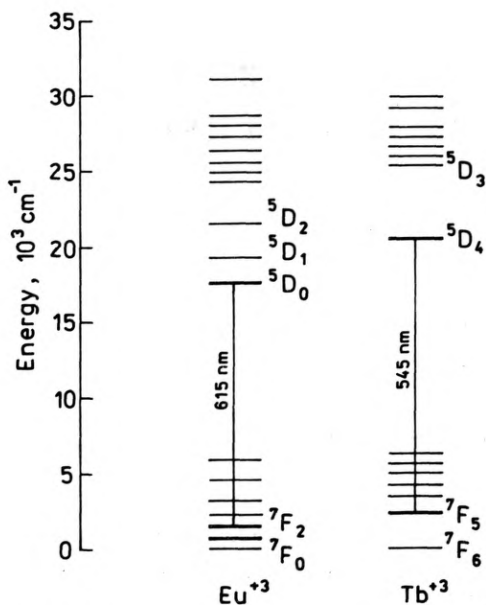


Fig. 1. Schematic diagram of energy levels and principal emission lines of europium and terbium ions

The value of  $k_{\text{H}_2\text{O}}$  is much greater than those of the other components. The values of  $k_{\text{F}}$  and  $k_{\text{nr}}$  are comparable ( $0.11$ ,  $0.19 \text{ ms}^{-1}$ ) for Tb(III) and ( $0.19$ ,  $0.25 \text{ ms}^{-1}$ ) for Eu(III), respectively, [4], [5], while a greater value of  $k_{\text{obs}}$  for Eu(III) ( $9.5 \text{ ms}^{-1}$ ) than for Tb(III) ( $2.5 \text{ ms}^{-1}$ ) results from the smaller energy gap between the lowest excited (emitting) state and the highest level of the ground manifold, in the case of Eu(III) [5], see Fig. 1. Replacement of the O-H oscillators ( $3500 \text{ cm}^{-1}$ ) by O-D ones, in deuterated media, causes the vibronic coupling with the O-D oscillators ( $2800 \text{ cm}^{-1}$ ) to become much less efficient. In  $\text{D}_2\text{O}$  solutions, Eq. (1) reduces to

$$k_{\text{obs}} = k_{\text{F}} + k_{\text{nr}}. \quad (2)$$

Since the radiationless deexcitation path exhibits a large isotope effect, combination of Eqs. (1) and (2) leads to

$$k(\text{H}_2\text{O}) - k(\text{D}_2\text{O}) = k_{\text{H}_2\text{O}}. \quad (3)$$

The measured difference  $\Delta k_{\text{obs}} (=k_{\text{H}_2\text{O}} - k_{\text{D}_2\text{O}})$  in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  is related to the number of water molecules coordinated in the first solvation sphere  $n$

$$\Delta k_{\text{obs}} = Cn \quad (4)$$

where  $C(=1/C_{\text{Ln}})$  is a constant specific for a given Ln(III) ions. Rearrangement of this equation gives

$$n = C_{\text{Ln}} \Delta k. \quad (5)$$

HORROCKS and SUDNICK [4], [5] have studied several crystalline solids and

solutions and have determined  $C = 1.05$  for Eu(III) and  $C = 4.2$  for Tb(III). The uncertainty of the  $n$  values determined by this method is  $\pm 0.4$ . A good correlation has been found between solid-state and solution results, proving that the quenching efficiency is independent of the state of the medium [2], [5]. The extensive work by HORROCKS *et al.* [4], [5] showed that measurement of luminescence lifetimes in both  $H_2O$  and  $D_2O$  is a useful method to determine quantitatively the number of water molecules coordinated to Eu(III) or Tb(III) ions in aqueous solution. The luminescence lifetime measurements of these ions have been successfully applied to explain the residual hydration numbers when these ions are complexed. The knowledge of hydration numbers has been used, in numerous applications, to interpret the binding mode in chemical and biological systems [2]–[10].

## 2. Experimental

### 2.1. Reagents

The solution of europium perchlorate was prepared by dissolving the  $Eu_2O_3$  in perchloric acid. For the studies in  $D_2O$  the Eu(III) solutions were made by successive evaporation of perchlorates to dryness and redissolution in  $D_2O$  to eliminate  $H_2O$  to an insignificant level. The pH was adjusted with  $HClO_4/DClO_4$  or  $NaOH/NaOD$  and had a final ionic strength 0.1 M  $NaClO_4$ . All samples containing  $D_2O$  solutions were protected with parafilm to avoid absorption of moisture from the air.

### 2.2. Instrumentation

Measurements of luminescence lifetime of Eu(III) in aqueous solution ( $H_2O$  and  $D_2O$ ) were carried out with the use of the detection system shown in Fig. 2.

Europium(III) ion was excited to a higher electronic level by a pulse laser beam at the wavelength of 395 nm. This resulted in emission from the  $^5D_0$  luminescent excited level to the ground  $^7F_3$  manifold. The 395 nm pulsed laser beam of spectral width,  $\Delta\lambda = 0.1 \text{ \AA}$ , was obtained from a tunable dye laser working on LD 390 laser dye pumped by pulses from a nitrogen laser (KB 6211, Cobrabid, Poznań, Poland).

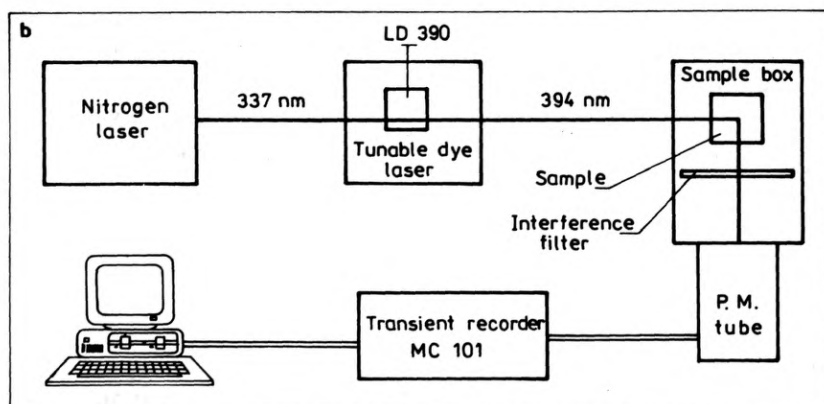


Fig. 2a

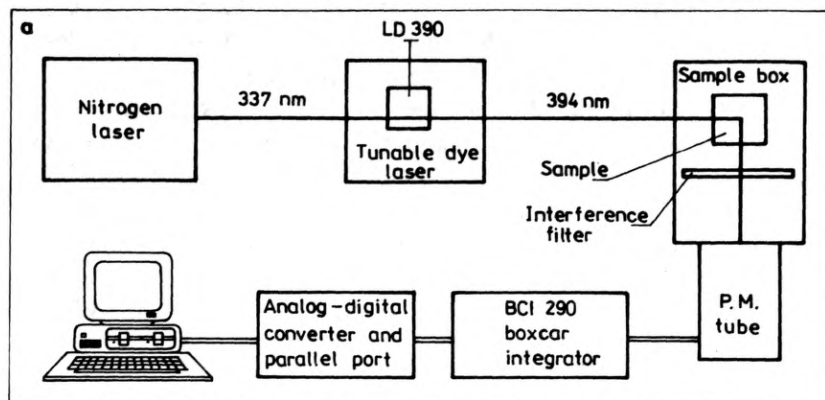


Fig. 2. Experimental setup for Eu(III) luminescence lifetime measurements applying: a – boxcar integrator, b – transient recorder

The LD 390 dye (Exciton Chemicals) was solved in spectrofluorimetric grade methanol (Merck). The beam from the dye laser had the typical pulse energy  $\sim 10 \mu\text{J}$  with the duration time of 5 ns. The samples were contained in a standard 1 cm quartz cell within a dark box and the experiments were conducted at room temperature. The emitted light of 615 nm was detected at 90 degrees to the exciting beam by a M12 FVC 51 photomultiplier tube. The scattered light was cut off using an interference filter. An electric signal from the PM tube was fed into the BCI 280 boxcar integrator, taking into consideration the photomultiplier linearity (particularly in the case of strong and long-lived signals in deuterated water solutions). A characteristic detail of the boxcar integrator used is that the input gate delay is digitally fed into a computer, while the amplitude value is given in the analog form. The collected data were entered into an IBM PC computer using a dedicated interface, made of an analog-digital converter and a parallel port. The measurement control and data collection were accomplished by means of the "Boxcar" computer procedure, settled especially for this purpose. Alternatively, a transient recorder MC 101 (Mescomp) for recording the luminescence decays was used. The transient recorder was based on the 8-bit flash analog-digital converter of 50 ns conversion time. The advantage of this device, compared with the boxcar integrator, is that the entire decay curve can be registered after one excitation pulse. Besides, the system makes it possible to average over many pulses. The luminescence decays observed in this experiment were analysed as single exponentials. The luminescence decay constants ( $k = \tau^{-1}$ ) were obtained using the least-square method for logarithms of amplitude values.

### 3. Results and discussion

Aiming at obtaining the best possible accuracy of results, special experiments testing the detection system were performed. At first, the time constant of the input of the

detection system, dependent on the input impedance of the boxcar integrator or transient recorder, as well as on the capacity of the coaxial cable connecting the photomultiplier tube with the recorder, was optimized. High input impedance permits obtaining higher voltage signal, however, may lead to elongation of the lifetimes measured. The time constant chosen to meet the condition of  $RC < \tau/100$  does not affect the lifetime measured and ensures that the signal amplitude is relatively high.

Accuracy of the estimated decay rate depends on the quality of the collected experimental data. Both devices used provide the possibility to average the measured signals over several laser pulses, increasing in that way the accuracy of data at the expense of the measurement time. Boxcar integrator creates the integral over the time of opening of the input gate

$$U_{\text{out}} \sim \int_{t_1}^{t_2} U_{\text{in}}(t) dt \quad (6)$$

where  $t_1$  and  $t_2$  denote the instants of opening and closing of the input gate, respectively. The average value  $\overline{U_{\text{out}}}$  over the required pulse number can be obtained.

In the case of transient recorder the measurements are carried out in the real time (sampling time 50 ns); the averaging procedure boils down to calculation of an arithmetic mean over many runs at each time point. Influence of averaging on the shape of the collected data is presented in Fig. 3. The upper curve shows the shape of the amplitude signal obtained using transient recorder after averaging over 32 pulses, whereas the lower one — over 2 pulses. Dependence of the correlation coefficient  $R^2$  of the data to the measured curves on the number of averagings is shown in Fig. 4.

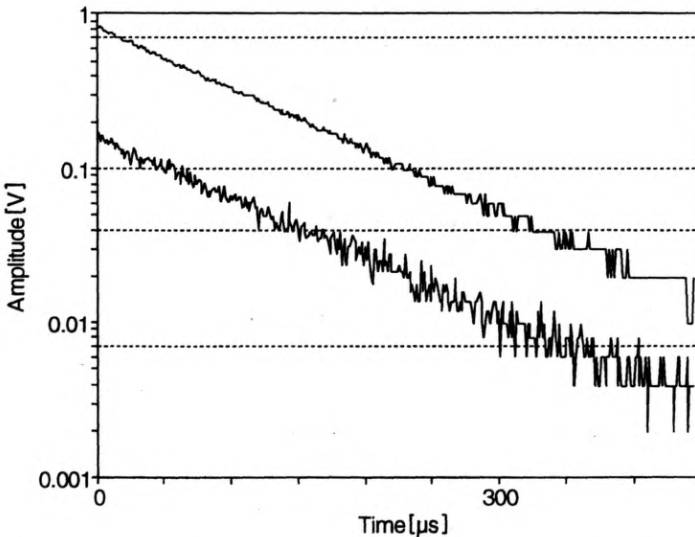


Fig. 3. Exemplary curves of the shape of the amplitude signal vs. time. For explanation, see the text

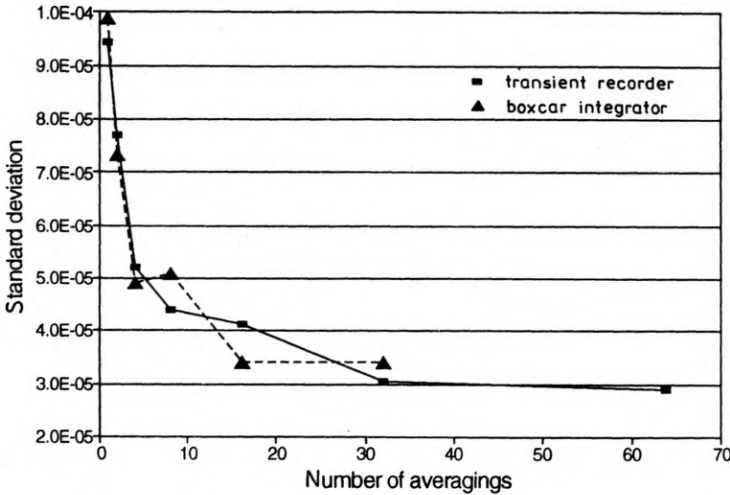


Fig. 4. Dependence of the standard deviation of the decay constant ( $k = 1/\tau$ ) on the number of averagings

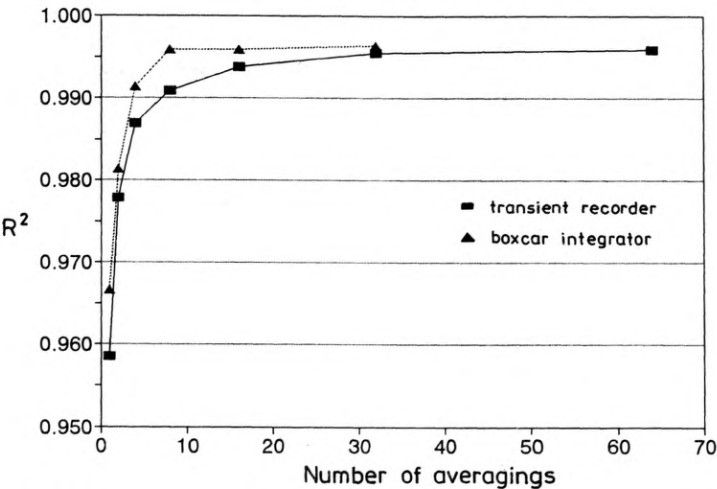


Fig. 5. Correlation coefficient  $R^2$  of collected data as a function of the number of averagings

Figure 5 presents a standard deviation of the luminescence decay constants  $k = 1/t$  as a function of the number of averagings. In the case of a small number of averagings, the accuracy ensured by the boxcar integrator is slightly better which is a consequence of integrating over the gate width. Beginning from 32 averagings both methods provide results of practically the same accuracy. An advantage of using the transient recorder in comparison with the boxcar integrator is much shorter time of measurements. An accuracy of the estimated decay constants depends mainly on the statistical spread obtained in many runs, which is caused by the differences in preparation of the samples or instabilities of the exciting system. The error resulting

from the inaccuracy of the detection system is negligible. The procedure described for luminescence lifetime measurements of Eu(III) is widely applied by us to determination of the hydration number of europium in various complexed systems.

Table. Luminescence lifetime of Eu(III)

| In H <sub>2</sub> O         |                               |                    |
|-----------------------------|-------------------------------|--------------------|
| $\tau$ [ $\mu$ s]           | $k$ [ $\mu$ s <sup>-1</sup> ] | Standard deviation |
| 111.7                       | 0.00895                       | 0.00005            |
| 111.4                       | 0.00898                       | 0.00004            |
| 110.3                       | 0.00906                       | 0.00009            |
| 109.7                       | 0.00911                       | 0.00010            |
| 111.6                       | 0.00896                       | 0.00008            |
| 112.0                       | 0.00893                       | 0.00005            |
| 106.9                       | 0.00936                       | 0.00004            |
| 109.5                       | 0.00913                       | 0.00007            |
| 109.6                       | 0.00912                       | 0.00003            |
| 110.1                       | 0.00908                       | 0.00003            |
| 109.2                       | 0.00916                       | 0.00003            |
| 110.2                       | 0.00907                       | 0.00002            |
| $\tau_{\text{avg}} = 110.1$ | $k_{\text{avg}} = 0.00908$    |                    |
| In D <sub>2</sub> O         |                               |                    |
| $\tau$ [ $\mu$ s]           | $k$ [ $\mu$ s <sup>-1</sup> ] | Standard deviation |
| 3934                        | 0.0002542                     | 0.0000006          |
| 4035                        | 0.0002478                     | 0.0000015          |
| 3916                        | 0.0002554                     | 0.0000013          |
| 3912                        | 0.0002556                     | 0.0000007          |
| 3994                        | 0.0002504                     | 0.0000015          |
| 4098                        | 0.0002440                     | 0.0000015          |
| $\tau_{\text{avg}} = 3979$  | $k_{\text{avg}} = 0.0002513$  |                    |

The data obtained in this work for Eu(III) luminescence lifetime (as perchlorate, in H<sub>2</sub>O and D<sub>2</sub>O, pH = 1.00 ± 0.02) at various experimental conditions are shown in the Table. An average value of decay constants obtained for H<sub>2</sub>O system is 0.00907 ± 0.00011  $\mu$ s<sup>-1</sup> (average  $\tau = 110.1 \pm 0.4$   $\mu$ s), and for D<sub>2</sub>O is 0.0000251 ± 0.000004  $\mu$ s<sup>-1</sup> (average  $\tau = 3980 \pm 60$   $\mu$ s). A standard deviation has been calculated for the entire data set and it is higher than that calculated for a single measurement. An excellent agreement between our lifetime data and literature results for europium in both H<sub>2</sub>O and D<sub>2</sub>O systems is observed [1], [4]–[10].

#### 4. Comments

The system described enables measurements of luminescence lifetimes in micro- and millisecond ranges for all luminescent lanthanide ions, provided that a proper wavelength of exciting laser beam has been chosen.



Applying the transient recorder MC-101 in the system for lifetime measurements makes it possible to shorten the time of measurement.

The data obtained by us for Eu(III) luminescence lifetime (as perchlorate, in H<sub>2</sub>O and D<sub>2</sub>O, pH = 1.00 ± 0.02) are well consistent with other published results.

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