Time-Gated Separation of Lanthanide Luminescence

Introduction

The distinctive luminescence of lanthanide ions has long been a challenge for the spectroscopist. Methods to counter the extremely low absorption coefficients and luminescence quantum yields have concentrated on

- Protective ligands to reduce vibrational quenching effects by X–H moieties (X = O, N,…).
- Deuterated solvents (also to reduce quenching effects of X–H).
- Antenna chromophores for enhanced absorption (with later energy-transfer to, and luminescence by, the lanthanide).

Luminescence from these systems comprises a number of sharp and well-resolved bands with characteristically long lifetimes, roughly 10^{-6}–10^{-3} s, depending upon the degree of quenching. With an integrated phosphorimeter, the Spex® FluoroMax®-P allows convenient time-gated measurement of lanthanide systems. In this *Application Note*, two lanthanide complexes comprising an encapsulating complex with benzophenone antenna chromophore (L, see Fig. 1) and europium (Eu) or terbium (Tb) ions are investigated using time-gated spectroscopy with the FluoroMax®-P.

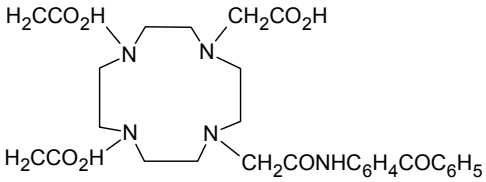

Figure 1. Benzophenone antenna chromophore, designated L in the text, complexed with Eu and Tb.

Experiment & Results

An excitation source (xenon lamp) flashes (~ 3 μs pulse-width). Detection of the sample's luminescence occurs within a time-window after the flash, according to a chosen delay time and detection-window size. Acquisition of a spectrum corresponding to any desired time-slice during the luminescence decay is possible. Luminescence lifetime measurements are made by recording the intensity of a specific wavelength with a chosen detection-window size and incremented delay time (Fig. 2).

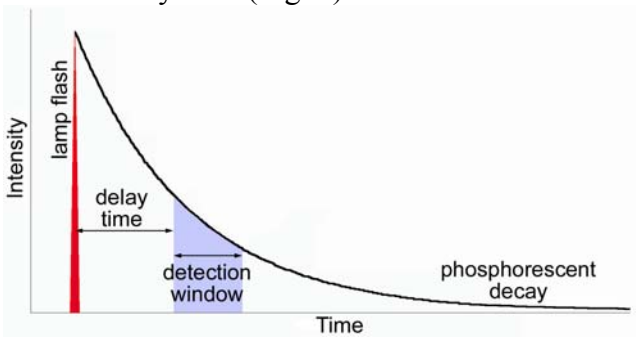

Figure 2. Schematic showing how time-gated measurements are performed.

The individual spectra of Tb-L and Eu-L complexes are shown in Figs. 3 and 4. The resulting luminescence spectrum from a mixture of Tb-L and Eu-L (Fig. 5) combines features from both Tb-L and Eu-L, acquired with a delay time of 0.01 ms, and sample window of 10 ms. Thus results from detection of *all* the luminescence from *both* species appear in Fig. 5. Time-gating allows a mixture of the two species to be spectrally separated, based on their different lifetimes (~ 0.60 ms for Eu-L, and ~ 1.1 ms for Tb-L).

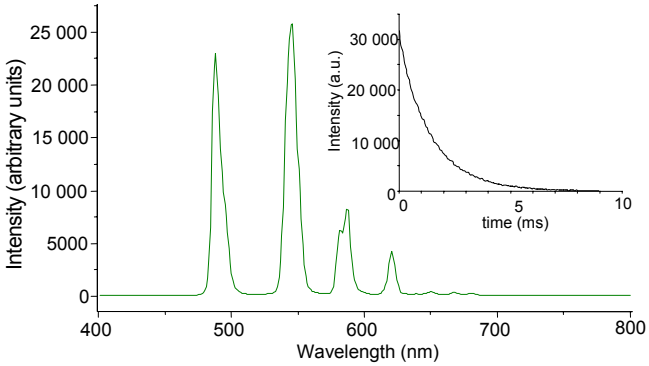

Figure 3. Luminescence spectrum and decay for Tb-L(*aq*). λ_{ex} = 295 nm; λ_{em} = 545 nm.

Careful choice of gating parameters allows spectra from this mixture to be obtained selectively from an early time (to minimize Tb-L and maximize Eu-L) and a late time (with negligible Eu-L, approximating pure Tb-L), as shown in Fig. 6. A time-gated matrix scan (Fig. 7) shows

the dependence of the spectral profile with time. A number of complete emission spectra were recorded while automatically incrementing the delay time between each run. The result is a 3-D array, with intensity, wavelength, and time information.

Conclusions

The Spex® FluoroMax®-P spectrofluorometer with integral flash-lamp can perform time-gated spectroscopic separation of mixtures of chemical species.

Acknowledgements

We thank Drs. Andrew Beeby and Gareth Williams of the Chemistry Department, University of Durham, UK, for useful discussion and preparation of the compounds studied herein.

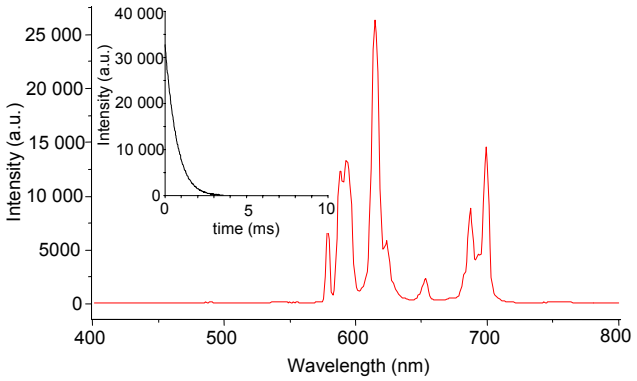

Figure 4. Luminescence spectrum and decay for Eu-L(*aq*). λ_{ex} = 295 nm; λ_{em} = 614 nm.

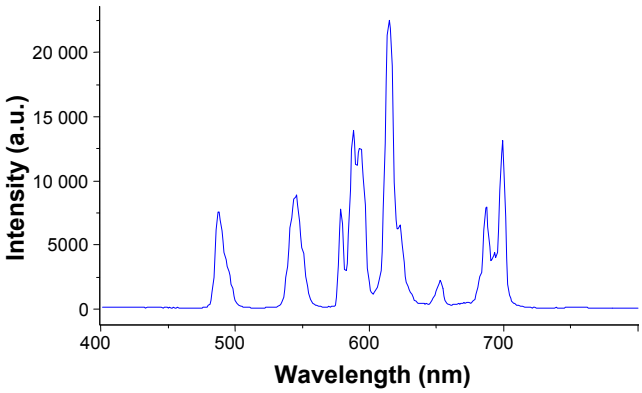

Figure 5. Luminescence spectrum for mixed aqueous Tb-L and Eu-L. λ_{ex} = 295 nm, delay = 0.010 ms, and sample window = 10 ms.

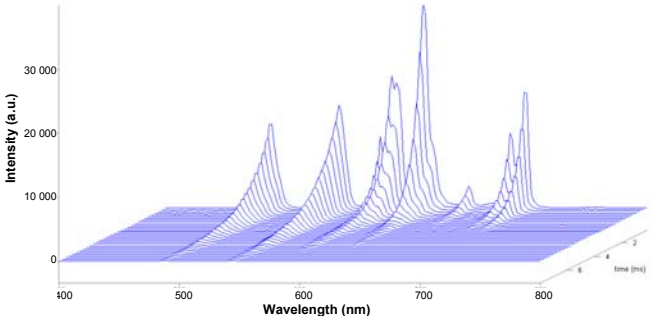

Figure 7. Time-gated matrix scan showing wavelength- and time-dependence of mixed aqueous Tb-L and Eu-L luminescence.

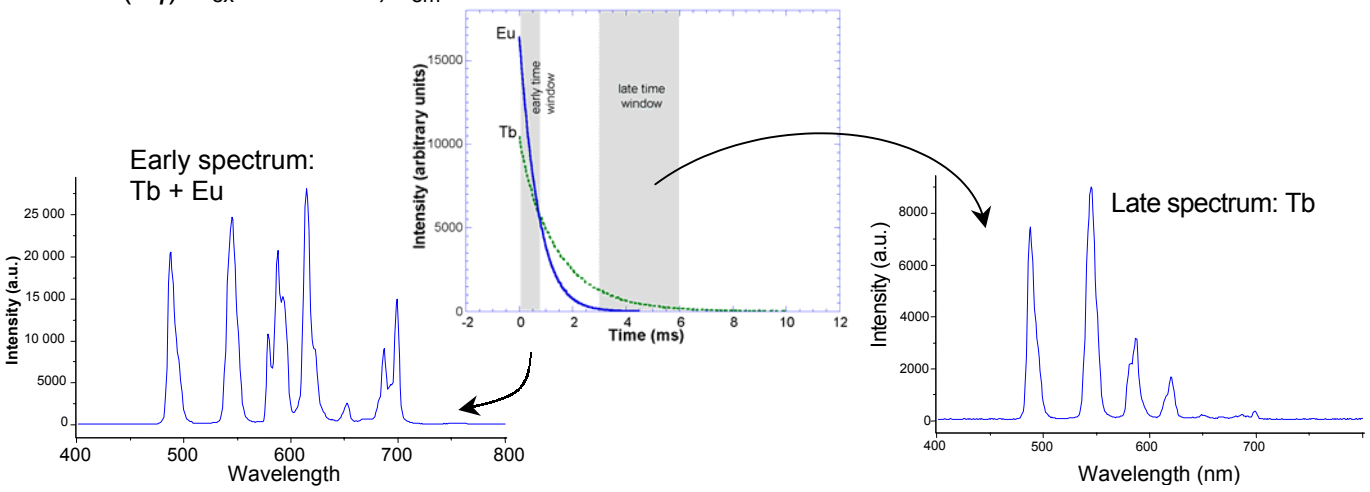

Figure 6. The principle of time-gated spectral separation for the mixture of Tb-L and Eu-L. The contribution from Eu-L is negligible in the spectrum recorded with the late time window.

In the USA:
Jobin Yvon Inc.
3880 Park Avenue, Edison, NJ 08820
Tel: +1-732-494-8660
Fax: +1-732-549-5157
E-Mail: fluorescence@jyhoriba.com
1-800-533-5946

In France:
16-18, rue du Canal
91165 Longjumeau cedex
Tel: +33 (0) 1 64 54 13 00
Fax: +33 (0) 1 69 09 93 19

Japan: +81 (0) 3 58230140
China: +86 (0) 10 6849 2216
Germany: +49 (0) 89 462317-0
Italy: +39 0 2 57604762
U.K.: +44 (0) 8204 8142