TECHNICAL NOTE

Measurement of Photoluminescence lifetimes in the µs Range

TN_P48; 31 May 2018, Maria Tesa, Anna Gakamsky, Stuart Thomson

Introduction

Edinburgh Instruments offers two types of photon-counting methods for time-resolved photoluminescence: Time-Correlated Single Photon Counting (TCSPC) for luminescence lifetimes between 5 ps and 50 µs, and Multi-Channel Scaling (MCS) for lifetimes between 1 µs and 10 s.

The working principle of TCSPC is explained in our previous technical note, "What is TCSPC?". In simple terms, a histogram of signal photon counts as a function of time is built from a series of START and STOP pulses that are input to the TCSPC electronics. Typically the START pulse is an electrical trigger synchronous to the optical excitation pulse, and the STOP pulse is caused by a single photon reaching the detector. The opposite case is known as reverse TCSPC, but for simplicity we will only focus on forward TCSPC here. The time between the START and STOP pulses is recorded accurately by the electronics, which acquire millions of START-STOP sequences in order to build a photoluminescence decay (Figure 1).

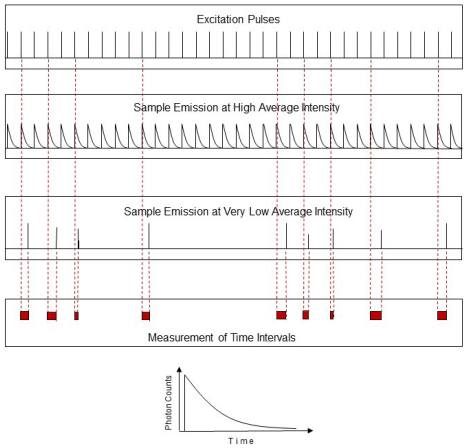

Figure 1: Schematic of TCSPC measurement. A source produces optical excitation pulses at a fixed repetition rate, and at the same time triggers the START of the TCSPC electronics. The excitation intensity must be fine-tuned to obtain a very low rate of detected photons (this is the STOP rate). The START-STOP delay is recorded by the electronics and a histogram of photon counts vs time is built.

In order to obtain reliable TCSPC data, the STOP rate must be kept at a low level (< 5% of the START repetition rate). This is known as the "pulse pile-up" limitation. Fortunately TCSPC electronics can operate at high repetition rates, up to 100 MHz, which makes the acquisition of short decays rather fast. However this restriction becomes an issue for luminescence lifetimes in the µs range: low START rates must be used meaning that a full decay with good statistics requires hours for acquisition. In addition, sometimes the dark counts on the detector itself contribute significantly towards pile-up. In both these cases, Multi-Channel Scaling offers a better alternative.

MCS is a single-photon counting technique that has lower temporal resolution than TCSPC, but no pulse pile-up restrictions. Photons reaching the detector generate pulses that are sorted into memory channels according to their arrival time. A histogram is built with a time resolution determined by the channel width (Figure 2).

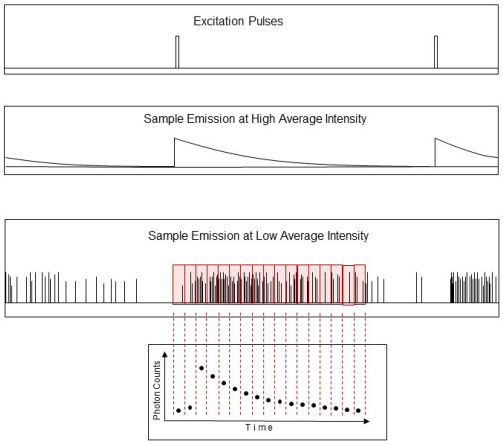

Figure 2: MCS measurement schematic. Emission photons are counted and assigned to time bins. The procedure is repeated after each excitation pulse to build a histogram of photon counts vs time, with the excitation pulse at the start.

The advantage of MCS is quick acquisition time: a decay in the µs range can be acquired in a few seconds. The disadvantage is that the minimum time resolution of MCS is 10 ns whereas TCSPC offers a minimum resolution of 305 fs.

Edinburgh Instruments spectrometers can be configured with TCSPC, MCS, or both; depending on your time resolution requirement. However configuring your instrument for fluorescence lifetime is not as simple as choosing the acquisition electronics. The measurable range of lifetimes depends not only on the electronics but also on the excitation source and the detector used. The width of the excitation pulse and the detector response time have a major effect on the instrument response function (IRF). These considerations are particularly important when the samples studied have multiple lifetimes across the ns and µs ranges; or when their lifetime is of the order of 500 ns – 5 µs, the crossover region between TCSPC and MCS.

In this technical note we present different examples of source and detection method combinations and show how the choice of configuration affects the measurement quality. Focusing on the FS5 and FLS1000 spectrometers, we introduce the new capability of EPL and EPLED pulsed diodes as MCS sources, which helps bridge the gap between TCSPC and MCS.

MCS with Pulsed µs Xenon Lamp

Both the FS5 and FLS1000 spectrometers offer the option of MCS with a pulsed µs xenon flashlamp. The flashlamp is coupled to the excitation monochromator so it is possible to tune the excitation wavelength. The lamp power is 5 W (FS5) or 60 W (FLS1000) and its pulse width is ~ 1 µs (pulse width values are slightly different between flashlamps).

TECHNICAL NOTE

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Thanks to its wavelength tunability and high power, the µs lamp and MCS electronics are the best option for photoluminescence lifetimes > 10 µs. An example luminescence decay is shown in Figure 3.

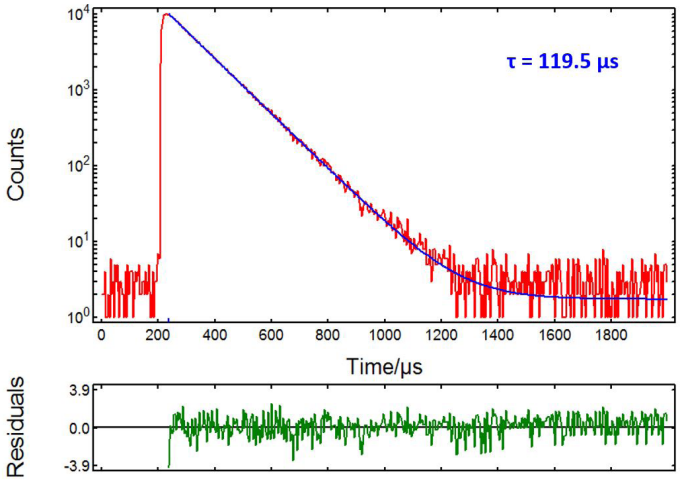

Figure 3: MCS decay of europium in 1% HNO_3, acquired in an FLS1000 Photoluminescence Spectrometer with a µs Xe lamp as the excitation source: experimental decay (red), tail fit result (blue), residuals (green). Measurement parameters: Repetition rate = 100 Hz, λ_{ex} = 339.5 nm, $\Delta\lambda_{ex}$ = 1.5 nm, λ_{em} = 592.3 nm, $\Delta\lambda_{em}$ = 1.5 nm, Resolution = 4 µs/channel, Acquisition time = 53 seconds.

With this configuration, photoluminescence lifetimes < 10 µs require the use of reconvolution fitting, so the IRF of the instrument needs to be recorded. However the fit becomes challenging when the lifetime is shorter than the width of the IRF. An example of this case is shown in Figure 4. The sample should present a single exponential decay with τ ~ 360 ns. However the fit to one exponential using this technique is beyond the limit confidence due to the lamp's pulse width, and therefore is not suitable for this sample.

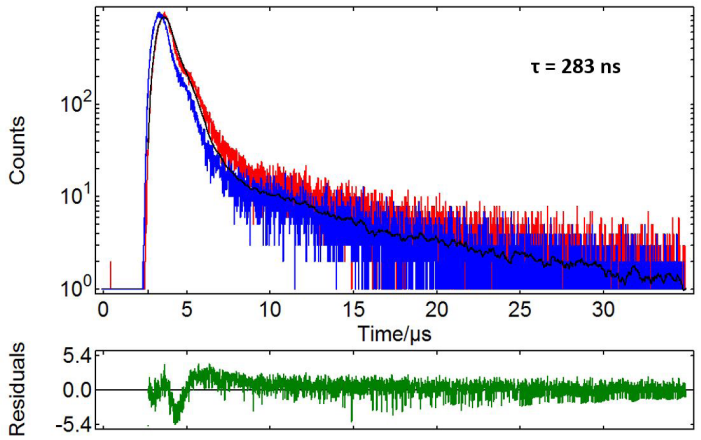

Figure 4: MCS decay of tris(bipyridine)ruthenium(II) chloride, $[Ru(bpy)_3]Cl_2$, in water using a µs Xe lamp as the excitation source in an FLS1000 spectrometer: experimental decay (red), IRF (blue), reconvolution fit result (black), residuals (green). Measurement parameters: Repetition rate = 100 Hz, λ_{em} = 610 nm, $\Delta\lambda_{em}$ = 5 nm, Resolution = 10 ns/channel, Acquisition time = 454 seconds.

In cases like this shorter excitation pulses are needed; for example a diode laser may be used. Edinburgh Instruments offers diode lasers with pulse widths < 200 ps (EPL series) and LEDs with pulse widths < 1 ns (EPLED series). They can be combined with either TCSPC or MCS acquisition electronics. The choice depends on experimental requirements such as signal strength, acquisition time, and time resolution.

TCSPC with EPL or EPLED Source

In TCSPC, the repetition rate is set by the pulsed source. Edinburgh Instruments EPL and EPLED sources have a wide range of repetition rates and allow acquisition in various time ranges (Table 1). Such wide range of time resolution is one of the key advantages of TCSPC.

Figure 5 shows a TCSPC decay of $[Ru(bpy)_3]Cl_2$. The luminescence lifetime is obtained easily without reconvolution fitting. One drawback of this technique is the acquisition time, which can be shortened by using MCS as the acquisition method.

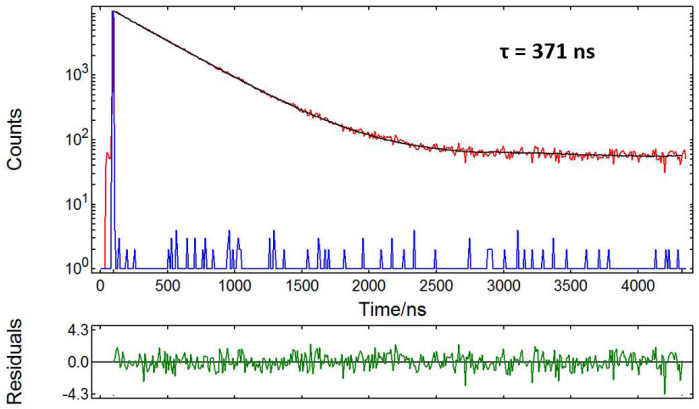

Figure 5: TCSPC decay of $[Ru(bpy)_3]Cl_2$ in water using an EPL-405 in an FLS1000: experimental decay (red), IRF (blue), tail fit result (black), residuals (green). Measurement parameters: Repetition rate = 200 KHz, λ_{em} = 610 nm, $\Delta\lambda_{em}$ = 5 nm, Resolution = 10 ns/channel, Acquisition time = 1057 seconds.

MCS with EPL or EPLED Source

Combining a short-pulse source with MCS electronics is the best option when the lifetimes are below the measurable value for the µs Xe lamp, but fast data acquisition is desired. The pulse pile-up condition does not apply in MCS which allows the excitation power of the laser to be increased.

The example in Figure 6 is a luminescence decay of $[Ru(bpy)_3]Cl_2$ acquired as above but using MCS instead of TCSPC. The time resolution is the same and therefore the data quality is not affected. The difference is in the acquisition time: 1057 seconds for TCSPC and 292 seconds for MCS. This becomes a huge advantage when several decays are acquired in sequence, for example in Time-Resolved Emission Spectroscopy (TRES) maps: the user can save hours of acquisition by switching to MCS.

TECHNICAL NOTE

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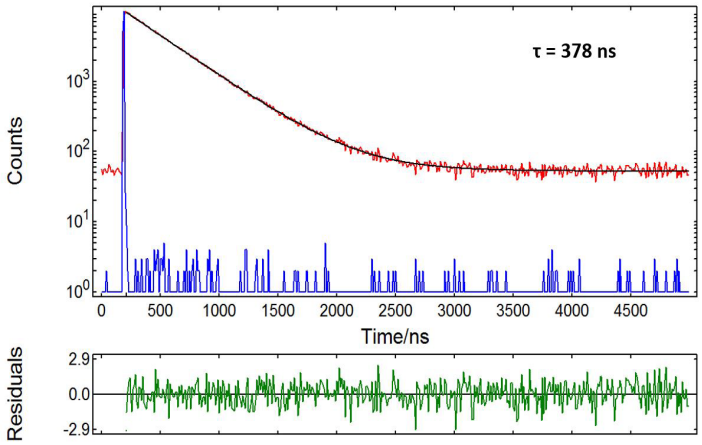

Figure 6: MCS decay $[Ru(bpy)_3]Cl_2$, in water using an EPL-405 in an FLS1000: experimental decay (red), IRF (blue), tail fit result (black), residuals (green). Measurement parameters: Repetition rate = 200 KHz, λ_{em} = 610 nm, $\Delta\lambda_{em}$ = 5 nm, Resolution = 10 ns/channel, Acquisition time = 292 seconds.

	Repetition Rate	Excitation Pulse Width	Time Resolution	Recommended Average Lifetime
MCS with us lamp	0.1 Hz – 100 Hz	1 µs	10 ns – 400 ms	10 µs – 1 s
MCS with EPL/ EPLED	0.1 Hz – 1 MHz	60 – 200 ps (EPL) 800 – 1000 ps (EPLED)	10 ns – 400 ms	100 ns – 1 s
TCSPC with EPL/ EPLED	2.5 KHz – 20 MHz	60 – 200 ps (EPL) 800 – 1000 ps (EPLED)	305 fs – 195 ns	50 ps – 100 ns

Table 1: Summary of time range, resolution and recommended lifetime ranges for TCSPC and MCS modes.

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