

# A Portable Apparatus for High Resolution Time Resolved X-ray Excited Optical Luminescence (TRXEOL) at the CLS

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## Introduction

TRXEOL is part of an ongoing development at the CLS and it is becoming an established method to study optoelectronic materials and materials for fast X-ray detectors and contemporary display technology. A review, outlining the essentials and state of knowledge of TRXEOL and its developments at synchrotrons has been recently published [1]. The detection equipment used in TRXEOL experiments are based on

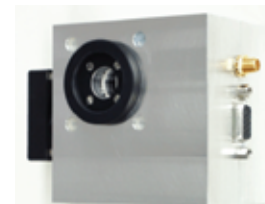
conventional detection apparatus such as NIM modules. These modules are inconvenient for non-expert general users to operate to reach the potential of their TRXEOL experiments. The Saskatchewan Structural Sciences Centre (SSSC) successfully transferred the technology that it uses for Time Correlated Single Photon Counting (TCSPC) and Fluorescence Lifetime Imaging in its Laser Technology Laboratory to the CLS for TRXEOL detection. This TRXEOL apparatus is compact, portable and can be setup with relative ease (replacing the laser with a synchrotron light source). Because of the advanced state of signal detection of laser based equipment, this TRXEOL is faster, provides higher resolution, and is equipped with real time data analysis capability. The resolution is high enough for the machine group at the CLS to monitor the quality of bunches delivered at the beamlines over time.

## Instrumentation

Single bunch synchrotron radiation excited XEOL is selected over a narrow wavelength range, and detected using a photon counter. The signal is assigned an arrival time relative to the excitation pulse in order to record its time-based decay. Photons are collected with either the lens system of a camera (Optronic OL610) or a collimator in the vacuum chamber and then to a fibre optic which guides the light to a CM110 Monochromator (Figure 1a). This 1/8 meter monochromator, (stray light <math>10^{-5}</math>,  $f/\#$  3.9, focal length 110 mm) was obtained from Spectral Products. A second fibre optic could be used to collect the light exiting the monochromator or the PMT can be directly mounted at the exit of the monochromator for increased light detection. The CM110's dual grating option allows for quick change between the 1800 gr/mm, 400 nm blaze holographic grating (12 nm bandpass) and the 600 gr/mm,



(a)



(b)

Figure 1: (a) CM110 Monochromator and (b) PMC-100-4 detector

500nm blaze ruled grating (36 nm bandpass), as experiments dictate.

The single photon detector, a PMC-100-4 is from Becker and Hickl (Figure 1b); it is suitable for wavelength detection from 185 to 820 nm with instrument response of below 200 picoseconds (FWHM). This Peltier cooled detector's dark count is 40 counts per seconds and it is capable of a continuous count rate greater than 5 MHz. It has an internal preamplifier (GHz) and an internal high voltage generator.

The SPC-630 data acquisition board (Figure 2) for the TCSPC technique (Becker and Hickl) uses two CFDs for signal processing and a time to amplitude converter (TAC) for time assignment of the arrival of the detected photons. The board is capable of an electrical time resolution down to 8 picoseconds,



Figure 2: SPC 630 board

FWHM, and 5 picoseconds, RMS, while its channel resolution can be as low as 813 femtoseconds with up to 4096 channels per curve. Its TAC can range from 50 ns to 2  $\mu$ s and its analog to digital converter is capable of error correction. The dead time of the board is 125 ns. The maximum number of counts per channel is  $2^{16}-1$  and the overflow can be corrected if desired. The synchronization channel can handle repetition rates from 0 to 200 MHz.

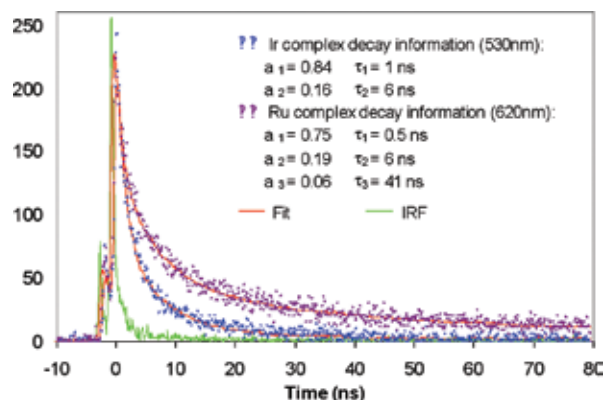
## Experimental Considerations

In any TRXEOL experiment, it is important to measure the instrument response function (IRF) of the system. IRF is a description of the temporal distribution of photons that incorporates the excitation pulse characteristics and any effect due to the light collection system, the detector's transit-time spread, all for a given TAC setting. This function is typically acquired using a scattering medium, but when the detector's wavelength range is not compatible, the excitation pulse-shape mimic technique is used [2]. Good IRF allows for better deconvolution of the decay curves recorded, especially for shorter lifetime components. Resolution can be severely limited by the presence of excitation peaks on the shoulders of the main excitation peak. This can be corrected by fitting and deconvolution.

In our test experiment, TRXEOL was measured at the SGM beamline 11ID-1 during a couple of single bunch runs (8 mA current at injection, 900 (FWHM) ps pulse width, 570 ns repetition rate) using Ir(ppy)<sub>3</sub> and Ru(bipy)<sub>3</sub> as the light emitter. The detector response function is well below that of the X-ray pulse. The incident beam slit was selected to ensure that the detector recorded events at less than 0.5% of the excitation beam repetition rate. This avoided pulse pile-up while limiting the total exposure time needed for data acquisition [3]. A minimum of ten lifetimes between excitation pulses was used to allow the background of the decay signal to be sufficiently low. Traces were recorded over five lifetimes to enhance fitting for multiple lifetimes.

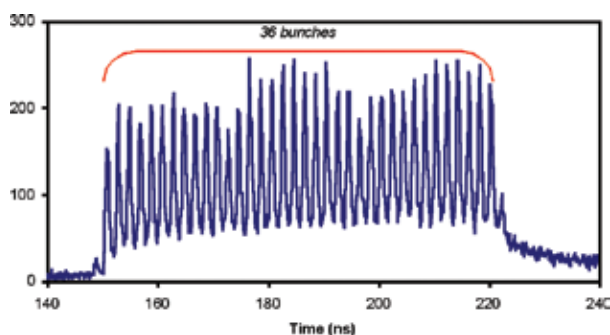
## Results and Discussion

Figure 3 shows the decay traces for Ir(ppy)<sub>3</sub>, Ru(bipy)<sub>3</sub> and a IRF. The IRF was obtained by burning the Ir(ppy)<sub>3</sub> sample in the X-ray beam for an extended period. The lifetimes obtained after IRF subtraction are different than those previously reported but are in the same order of magnitude. The high resolution data obtained from this experiment has a greater



**Figure 3:** Decay traces showing a good IRF and two TRXEOL data sets fitted to multiple lifetimes

degree of confidence and better fitting. It was also clear from our experiments that samples do undergo degradation in the X-ray beam. Although the XANES and the XEOL of the Ir(ppy)<sub>3</sub> sample did not change significantly in a short time, dramatic changes in the lifetime was observed. Other TRXEOL



**Figure 4:** Time spectrum of 36 bunches

apparatus cannot efficiently obtain high resolution data to show this feature of sample degradation.

The lifetime changes are associated with different decay channels and a high sensitivity to changes in the electronic and geometric structure of the sample. XANES and XEOL are sensitive to the changes at the *N* edge and in the bandgap. The TRXEOL is highly sensitive to slight changes in the environment. These changes range from slight changes in the temperature to small surface charging.

The time spectrum of 36 bunches at 2 ns apart are shown in Figure 4. This fill pattern reflects the machine characteristics at the beginning of a fill. The wings are approximately 5% of the main band and with time, the purity of bunches degrade to a level that the wings are approximately 30% of the main band. This issue is managed with injections at 4 hr intervals.

## Summary

We have established the protocol and a new apparatus for high resolution TRXEOL experiments at the CLS for general use. With this setup, it is possible to track sample degradation and beam degradation during measurements.

Our experiment shows that high purity bunches will increase the accuracy of data obtained from TRXEOL experiments and that high purity bunches could lead to a brighter source. Thus TRXEOL can benefit from machine development to meet the needs of brightness and high purity single bunch at the same time.

Fast detection can be developed as a diagnostic to monitor sample degradation during all types of measurements. This technique can be widely used for the study of any light emitting materials, from nanostructures to molecular beacons and soft matter.

## References

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