Ultra-Fast Fluorescence Decay in Scottish Whisky

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Abstract: Using TCSPC with ultra-fast hybrid detectors we found extremely fast fluorescence-decay components in Scottish whisky. Already cuvette based fluorescence measurements with picosecond-diode laser excitation showed that the decay functions contained components with lifetimes shorter than 50 ps. The relatively large width of the laser pulses and the transit time in the cuvette resulted in an IRF width of about 75 ps. Due to uncertainty in the IRF the component lifetimes could not be determined more accurately. We therefore used our DCS-120 MP multiphoton FLIM system to obtain fluorescence decay data at higher temporal resolution. Negligible excitation pulse width of the femtosecond laser, small effective sample volume, and absence of transit-time effects in the sample lead to an IRF width of about 25 ps. Data obtained with this system showed fast decay components down to less than 10 ps decay time and more than 90% amplitude. Decay times and amplitudes were clearly different for different whisky samples. Whether the values are characteristic of the brand or of the ageing we are not able to tell.

Cuvette-Based Measurements

For the cuvette measurements we used the normal 90° configuration [1]. The collimated laser beam of a bh BDS-SM 405 nm picosecond diode laser entered the cuvette from one side. The laser power was about 1 mW, the pulse repetition rate 50 MHz. The light leaving the cuvette under 90° was detected by a HPM-100-06 hybrid detector [3]. Scattered excitation light was blocked by a 420 nm long-pass filter. The light was delivered directly, without a lens, to the active area of the detector. The fluorescence-decay data were recorded by an SPC-150NX TCSPC module [1]. The number of time channels was 4096, the time per channel 1.22 ps. Decay curves recorded with this setup are shown in Fig. 1.

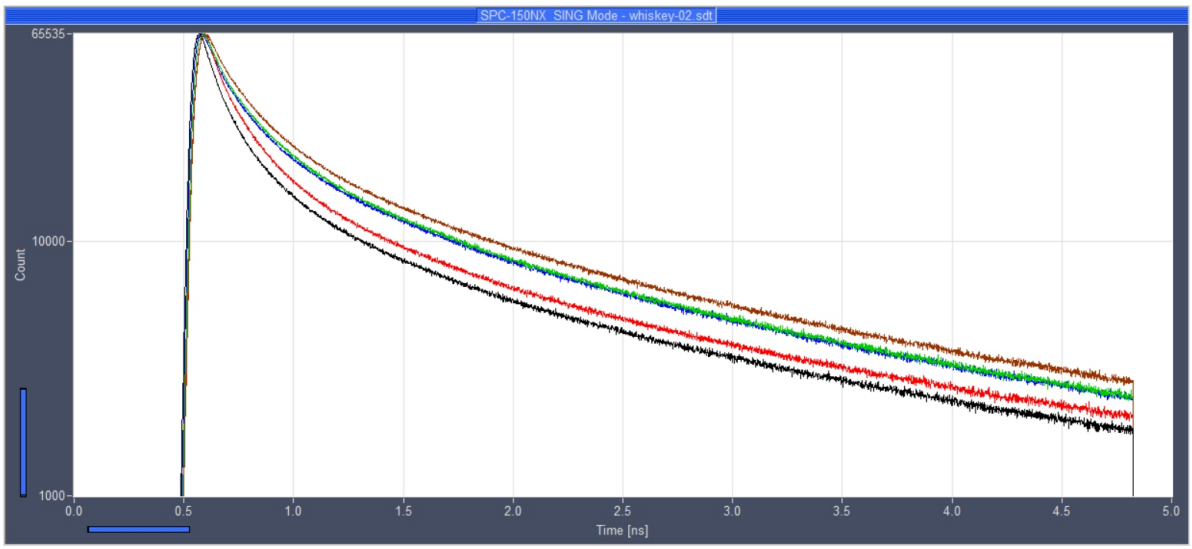

Fig. 1: Decay curve of different brands of whisky. Green, blue, red are Scotch, brown is an Irish, black is a Kentucky.

The blue, green and red curves were obtained from Jura, Ardbeg, and Lagavulin, respectively. For comparison, the brown curve shows an Irish whisky (Jameson), and the black curve a Kentucky whiskey (Seven Oaks). The general shape of the decay curves is the same for all brands. The decay

is multi-exponential, but can be reasonably fit with three exponentials. Differences between the brands appear to be more in the amplitudes of the components than in the lifetimes.

Fig. 2 shows a triple-exponential fit of the green decay curve (Ardbeg). The decay time for the fastest component, t1, comes out with 32 picoseconds, the amplitude with 67.6 %. It should be noted however, that t1 strongly depends on the width and the shape of the IRF. Unfortunately, the effective IRF in a cuvette-based system is poorly defined. It contains a component from the transit time of the laser pulse through the cuvette. For a 1-cm cuvette it is about 50 ps. This value changes, however, if a significant part of the laser power is absorbed. The fluorescence intensity is then different for different points along the laser beam path. Even an accurately measured IRF therefore does not necessarily represent the effective IRF of the fluorescence measurement. We therefore refused to measure an IRF and instead used the synthetic IRF of SPCImage NG [5], see green curve in Fig. 2. The best fit was obtained with an IRF of 74 ps width. The lifetime of the fast component, t1, is then 32 ps. However, with slightly different values of the IRF width almost any lifetime of the fast component from 40 ps down to 10 ps can be obtained.

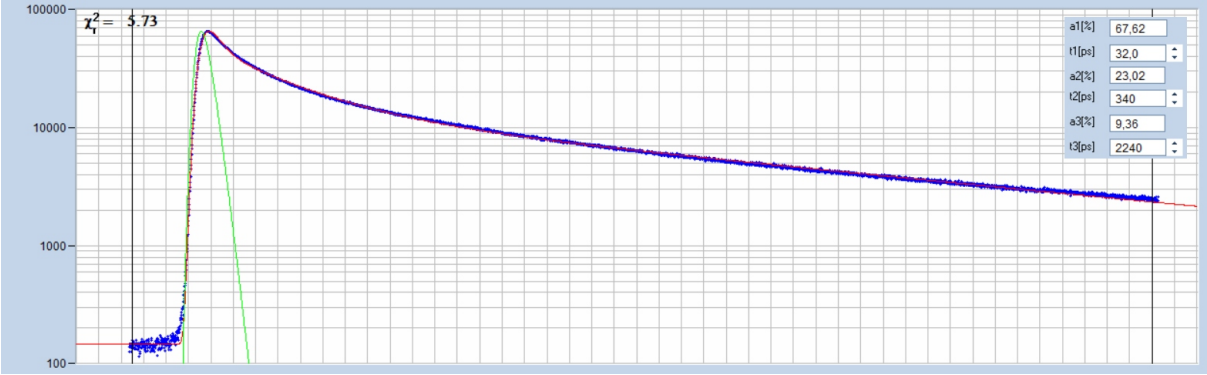

Fig. 2: Triple-exponential fit with SPCImage NG [5], measured in cuvette setup. Decay data from Ardbeg, green curve in Fig. 1. Decay curve shown blue, IRF green, fit with model function red. Horizontal axis 0 to 5 ns, 100 ps per division. The fastest component, t1, comes out with a lifetime of 32 ps and an amplitude of 67.6 %.

Two-Photon FLIM Measurements

For two-photon excited decay measurement we used the bh DCS-120 MP multiphoton FLIM system [2, 4]. A Toptica Femto-Fibre Pro laser was used as an excitation source. The laser delivers pulses of about 120 fs width at a repetition rate of 40 MHz. The laser delivers about 150 mW. Whisky samples were filled into standard cell dishes and imaged by the normal FLIM process [2]. The fluorescence light was detected by an HPM-100-06 hybrid detector via the non-descanned beam path of the FLIM system. An SP700 short pass filter blocked the excitation wavelength, possible SHG light was blocked by an LP420 nm long-pass filter. The laser power in the sample plane was reduced to 10 mW by the attenuator wheel of the DCS-120 scanner.

Decay data were acquired by scanning the samples with a frame format of 128 x 128 pixels, and a frame time of 0.4 seconds. In comparison to single-point measurement scanning produces larger data files but avoids temperature changes by the injected laser power. The decay data were recorded in 4096 time channels, into an observation-time interval of 5 ns, and with a time-channel width of 1.22 ps. The recorded data were analysed with SPCImage NG. Within the scan area, an ROI was selected which contained about 1 million photons. The decay data of the pixels within the ROI were combined into a single curve, which was then used for determination of the decay parameters.

A triple-exponential decay model was used to fit the data. Moreover, a synthetic IRF was generated by the IRF-modelling function of SPCImage NG [5]. IRF modelling delivered an IRF width of 24 ps, which is in good agreement with the values obtained in previous experiments [6, 7]. The IRF is not quite as fast as the IRF obtained with direct laser illumination of the detector (19 ps) [3]. We believe that the difference is due to transit-time differences in the NDD beam path. The optical path contains spherical lenses with short focal length. Spherical aberration of these lenses causes path length differences on the order of 1 mm from the centre of the beam path to the edge. 1 mm path length difference in water translates into 5 ps timing spread , which explains the differences in the IRF widths.

A decay curve obtained from Ardbeg whisky is shown in Fig. 3. The blue curve is the fluorescence decay, the green curve is the IRF, and the red curve is the model function. Residuals are shown at the bottom. Decay parameters are shown in the upper right. The decay function is dominated by an extremely fast decay component. A fit with a triple-exponential decay model delivers a fast decay component, t1, with a decay time of 9.2 ps, and an amplitude of 91.2 %. The amplitude-weighted mean lifetime is 55 ps.

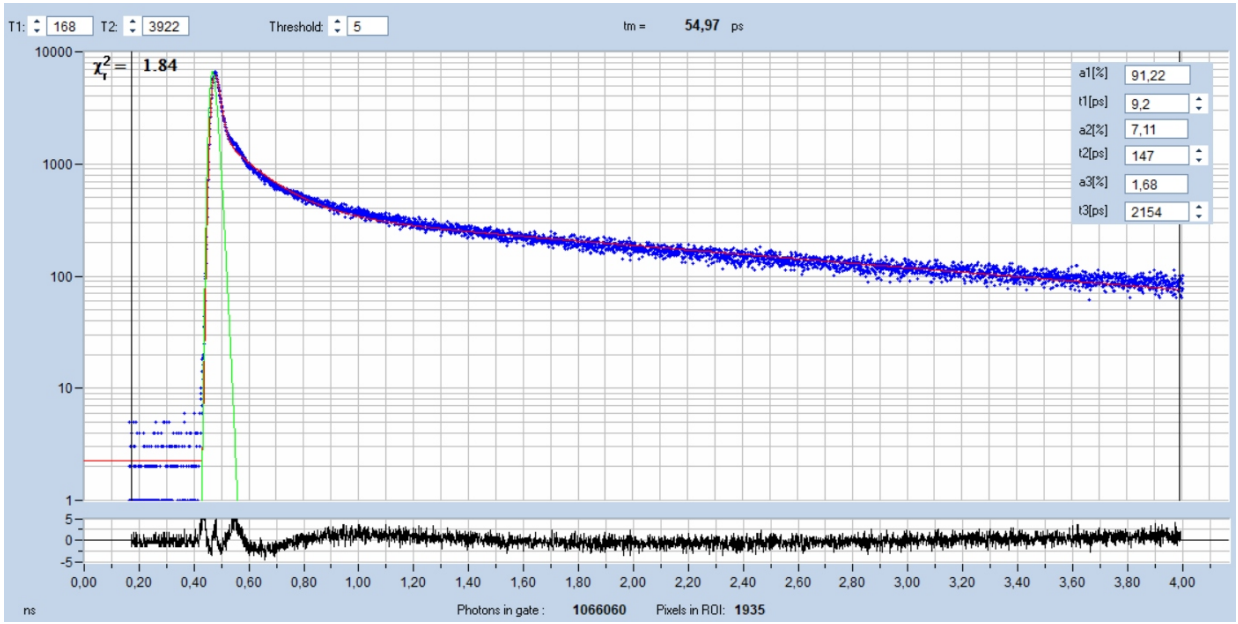

Fig. 3: Two-photon decay curve of Ardbeg Scottish whisky. The fluorescence decay curve is shown blue, the IRF green, and the model function red. The decay parameters are show upper right. The fast decay component, t1, has a lifetime of 9.2 ps and an amplitude of 91.2 %.

A comparison of the decay data of the different brands of whisky is given in Fig. 4. Visibly, the curves appear more or less 'steep', indicating that the major difference is in the fast decay component. The decay parameters confirm this: a1 decreases and t1 increases from Ardberg and Jura over McIntyre, Seven Oaks, Lagavulin, to Jameson. Because the decay is dominated by the fast component, also the amplitude-weighted mean lifetime, tm, follows the same tendency.

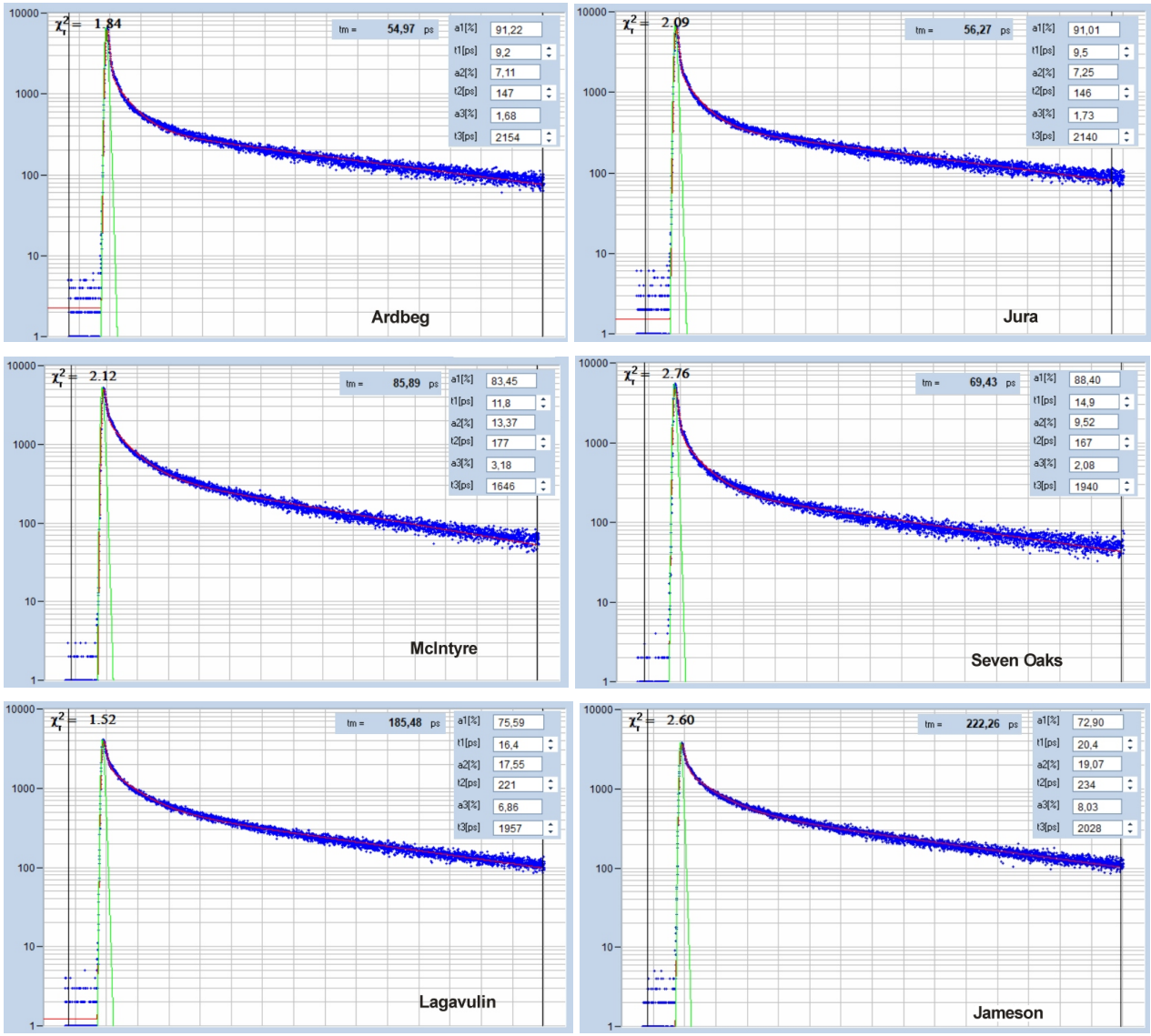

Fig. 4: Decay curves and decay parameters for 6 different brands of Whisky. Two-photon excitation at 780 nm, HPM-100-06 hybrid detector.

Summary

We used two-photon excitation with a femtosecond laser in combination with ultra-fast TCSPC FLIM to record fluorescence-decay functions in Scottish whisky. Due to the fast IRF of the system we were able to detect fluorescence-decay components down to lifetimes of less than 10 ps. The fast decay appears with an amplitude of up to 91 % and thus dominates the net fluorescence decay. Different brands of whisky noticeably differ in their fluorescence-decay behaviour. The differences are mainly in the lifetime and the amplitude of the fast decay component. Whether this is a result of the manufacturing process, the ageing, or the material of the barrels in which the whisky is stored, and whether the decay parameters are specific of the different manufacturers we do not know. More data are required to find that out. Whisky friends are welcome to send us their samples.

The most important result of this investigation is probably the confirmation that ultra-fast fluorescence-decay processes [6, 7, 8] are by far more frequent than commonly believed. Ultra-fast

decay times should therefore no longer be considered a peculiarity but a real source of scientific information.

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