

## Development of a fibre optic luminescence lifetime spectrometer

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**Abstract.** A spectrometer for measuring luminescence lifetimes has been developed. The design includes a bifurcated fibre optic cable for delivering the light from the source to the sample and from the sample to the detector. It uses a fast photomultiplier tube as the detector, a boxcar averager for data acquisition and a PC clone for data analysis. A nitrogen pumped dye laser is used as the light source and this has a pulse width of 1.2 ns. The spectrometer has been used to measure lifetimes from a minimum of 0.75 ns (rose bengal) to 597  $\mu$ s (solid uranyl nitrate hexahydrate).

A study has been made of the effects of concentration and temperature on the decay of uranyl ions ( $\text{UO}_2^{2+}$ ) in aqueous solution. The decay is found to be biexponential, except at temperatures above 60°C, where a three-component decay analysis gives the best results for matching the data to an Arrhenius Plot. The nature of the third emissive state, appearing at high temperatures is unknown and no spectroscopic state assignment has yet been made.

**Keywords.** Luminescence; lifetime spectrometer; uranyl; fibre-optic.

### 1. Introduction

There are three principal types of instrument for determining fluorescence lifetimes; namely the phase method (Voigtman 1986), the photon counting method (single photon counting, SPC) and the pulse sampling (stroboscopic) technique (Badea and Georghio 1976; Voigtman and Wineford 1986). The phase technique was the first method developed that was capable of determining lifetimes in the nanosecond range (Gaviola 1926), however, it is not a convenient method for studying complex kinetics (Ide *et al* 1983). The stroboscopic technique has remained largely unused, because of the problems of sensitivity using flashlamps, and data distortion due to impedance mismatch and RF pickup. The sampling technique is inherently more sensitive to these effects than SPC.

Although SPC has many advantages such as high sensitivity, easily available instruments from nuclear physics and an insensitivity to the shape of the detector's output (because only the rising edge is used), its disadvantage is that it makes inefficient use of the signal. This stems from the need to avoid "pile up" by detecting only a single photon for each excitation pulse, and is achieved by usually decreasing the count rate to about 1% of the excitation rate. Hence, sources with a repetition rate of  $10^4$  Hz or faster are used, excluding the use of a nitrogen laser.

The aim of the project was to develop a fibre optic luminescence lifetime spectrometer, that is capable of measuring sub-nanosecond lifetimes. This is because

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of the advantages of using optical fibres for remote detection (Malstrom and Hirschfield 1983; Newby *et al* 1984; Milanovich *et al* 1986) as well as for delivery of the excitation light to a small volume sample or to a specific site (Minami *et al* 1986). Optrodes (OPTical electRODES) would be preferable to electrically based sensors in many areas, especially in biomedical applications (Peterson and Vurek 1984; Peterson *et al* 1984; Tromberg 1984, 1987; Coburn 1985; Wolfbeis 1985).

The use of a fibre optic cable determines the other instruments used. For maximum efficiency of coupling the excitation light into the fibre, a laser with a collimated output, is many orders of magnitude more efficient than a subnanosecond duration flashlamp (Birch and Imhof 1981). A nitrogen pumped dye laser has the advantage of cost as well as an output in the ultra-violet (337 nm) where many fluorophores absorb.

Sampling oscilloscopes and boxcar averagers function by sampling a short portion or time slice within a repetitive signal, and with each repetition, the position of this time slice is moved so that eventually the entire curve has been sampled (Letzter 1983). A technique to increase the signal-to-noise (S/N) ratio is that of averaging, where the value of the signal at each time slice is enhanced by averaging over many repetitions and random noise is reduced (Ekindorf and Walters 1981). A transient digitizer, on the other hand, digitizes the entire waveform in a single shot, but also allows for improvements in S/N ratio by averaging. However, its drawback has been that it can only deal with low repetition rate signals with a lower time resolution, than is possible with other techniques.

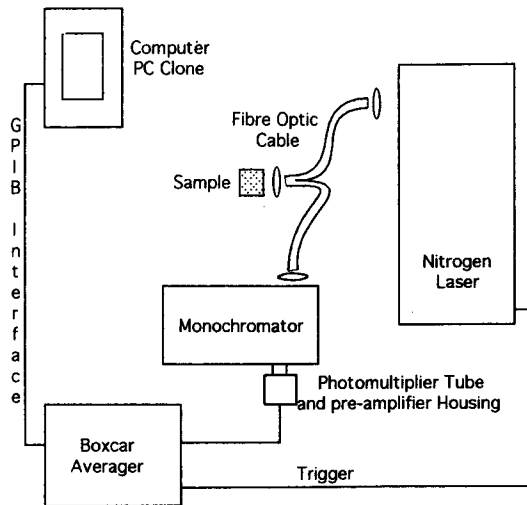
## 2. Equipment details

A luminescence lifetime spectrometer based on a stroboscopic technique has been developed along a modular concept, so that new technological advances could be easily incorporated. Figure 1 shows the experimental set-up, which consists of:

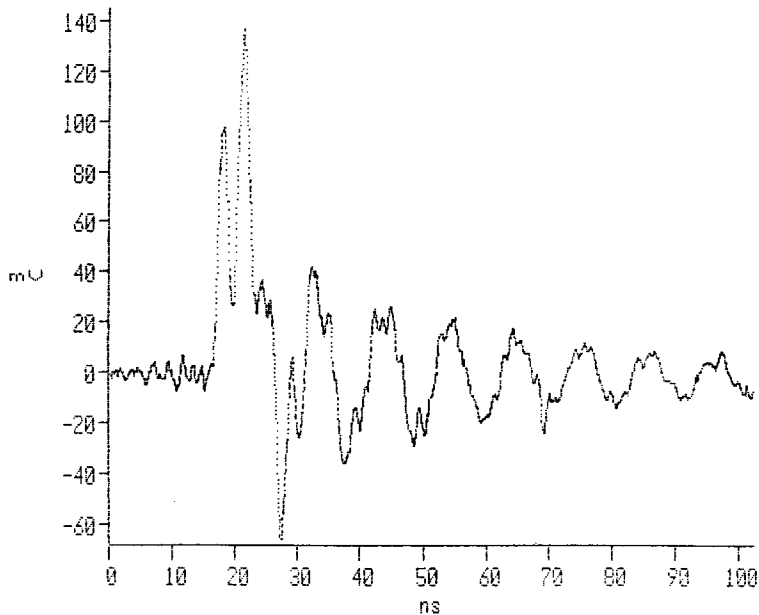
- (1) An EG & G nitrogen pumped dye laser, which has a specified FWHM pulse of 1.2 ns for the nitrogen laser output and 1 ns for the dye laser, with a maximum repetition rate of 100 pulses per second.
- (2) A bifurcated fibre optic cable for delivery of the excitation light to the sample and the fluorescence signal to the monochromator and detector.
- (3) A Hamamatsu R 1635 Photomultiplier detector (PMT), with a specified rise time of 0.8 ns and a gain of  $10^6$ .
- (4) A data acquisition using an EG & G model 4400 Boxcar Averager System, with a Tektronix Sampling Head of rise time of 75 ps (4.5 GHz bandwidth), or a gated integrator for slower phenomena.
- (5) A data analysis PC clone using software from IBH, originally developed for analysis of fluorescence lifetimes from SPC methods. The data is analyzed by a process of iterative re-convolution (Cline Love and Sharer 1985; Birch and Imhof 1985).

Unlike SPC methods, the entire time response from the detector is used in a stroboscopic technique, and so the fidelity of response from the detector is critical. Not only is a fast detector necessary (the criteria are, a fast rise time and a small FWHM to a delta impulse function), but it must have a clean response, with minimal effects from over/under shoot and afterpulsing (Coates 1973).

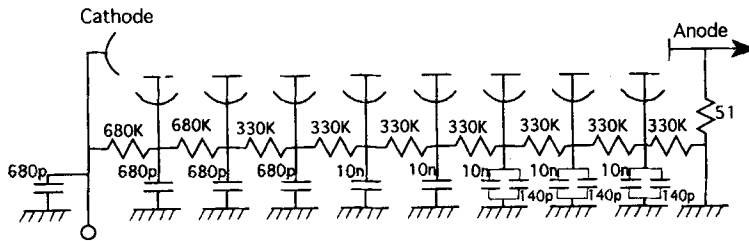
Whereas traditional methods of dynode chain layout and design are satisfactory for slower PMTs, such as the ubiquitous EMI 9661, modern PMTs such as Hamamatsu's R 1635 have such a fast response, that the lead lengths of the components are critical, and even a few millimeters can cause an impedance mismatch due to the inductance of the leads (see figure 2). The idea of using a Printed Circuit Board (PCB)



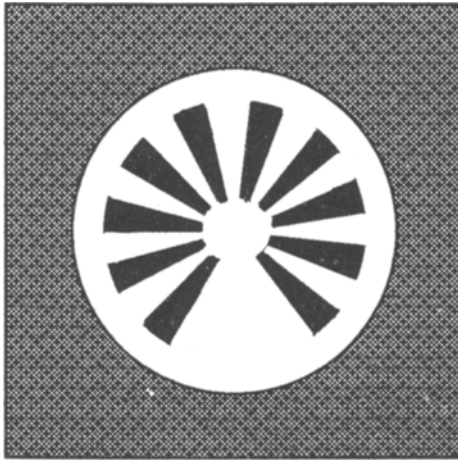
**Figure 1.** A schematic of the experimental set-up. Shown are the nitrogen laser, the bifurcated fibre optic cable, a monochromator with an attached photomultiplier tube housing, the boxcar averager and a PC clone for data analysis.



**Figure 2.** The output from a Hamamatsu R1635 photomultiplier tube, with the dynode chain components directly soldered onto the base, and with only three capacitors.



**Figure 3.** The dynode chain which gave the best results has capacitors connected directly to ground for the entire length of the dynode chain. This configuration ensures that any RF interference sees the capacitors as a direct short circuit to ground. Also, the capacitors ensure stability of voltage for the dynodes as large pulses of electron clouds pass by, acting as a charge source.

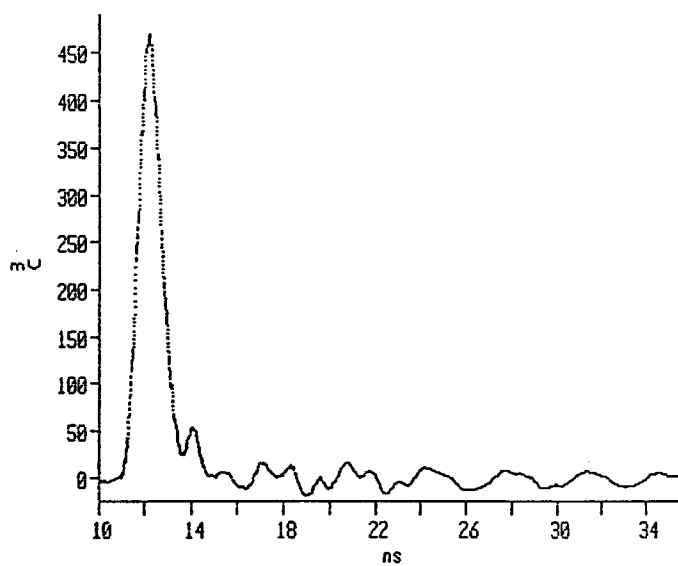


**Figure 4.** The actual size of the printed circuit board, onto which the dynode chain was soldered, measures  $45 \times 45$  mm.

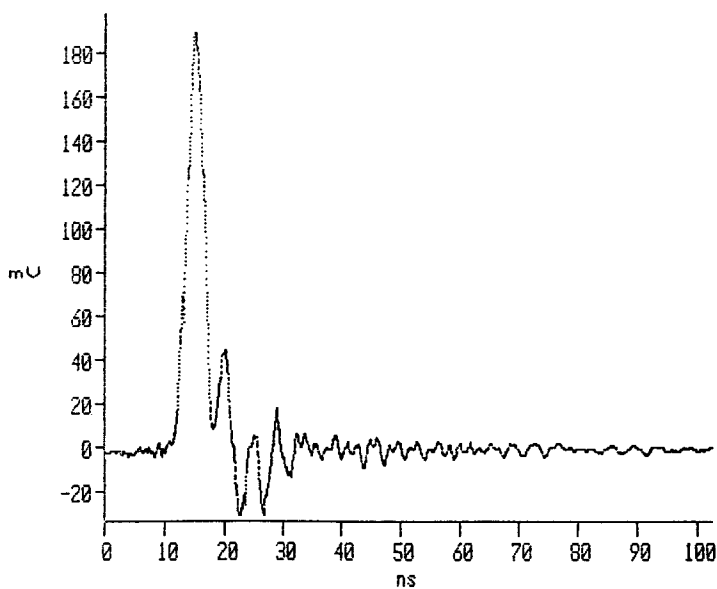
on which to layout the components for a dynode chain is not new (Beck 1976), but the choice of components and their positioning were found to be critical.

Figures 3, 4 and 5 show the dynode chain used, the PCB on which they were laid out and the response obtained. A comparison of figures 5 and 2 show the dramatic improvements that were achieved with the PCB, compared with directly soldering the components onto the PMT base. Figure 6 shows the results from Hamamatsu's own dynode chain design (E1761-04), and as can be seen this suffers from afterpulses. The important design features responsible for this improvement are:

- (a) Surface mounting the components so as to decrease the lead lengths to less than 1 mm per component.
- (b) The use of ceramic disc capacitors connecting each dynode to ground. This has the two-fold effect of giving the high frequency RFI (radio frequency interference) a direct path to ground, and providing a charge source to each dynode to minimize voltage fluctuations as the clouds of electrons being amplified, pass.



**Figure 5.** The final output for an impulse input of 1 ns FWHM, has a FWHM of 1.2 ns. This was obtained from the dye laser output, and by comparing with figure 7 (output for the nitrogen laser), it can be seen that the dye laser has a "clean" profile.



**Figure 6.** This is the impulse response obtained from Hamamatsu's own dynode chain for the R1635 photomultiplier tube.

The Hamamatsu R 1635 was tested for linearity of its output, by using neutral density filters to control the intensity of light falling on the cathode. The output from the PMT is found to be linear up to 800 mV, which is sufficient for the input signal channel of the boxcar averager without the need for a preamplifier.

### 3. Experimental results

#### 3.1 Instrument tests

The system's use of a fibre optic cable was first tested out by making measurements using both the fibre optic assembly and a sample chamber with telescopes and comparing the data. No difference was seen for the two sets of data.

The system was tested out and verified by measuring the lifetime of rose bengal. Figure 7 shows the nitrogen laser pulse, the decay profile and the solid line as a single exponential fitted function, formed by reconvoluting the measured excitation pulse with theoretical decays, and matching this to the fluorescence decay. The lifetime for rose bengal at a concentration of  $1 \times 10^{-5}$ , was  $0.75 \pm 0.02$  ns, which compares with other values of  $0.77 \pm 0.07$  ns (Vickers *et al* 1987).

#### 3.2 Uranyl

Uranium ions are one of the few rare earths which fluoresce in aqueous solution and it is the uranyl ion ( $\text{UO}_2^{2+}$ ) which is responsible for this fluorescence. This species has been of interest since the Manhattan Project (Dieke and Duncan 1949) and has been studied in depth, but because of its complex photophysics very little is known.

Its decay lifetime varies from  $597 \pm 52 \mu\text{s}$  for the solid hexahydrate uranyl nitrate, down to about  $2 \mu\text{s}$  in aqueous solution. Arguments have arisen as to whether the decay is fluorescence or phosphorescence (Bell and Biggers 1965; Gorler and Wabrand 1972), but Jorgensen (1982) argues that distinctions between singlet and triplet states for the uranyl ion are not significant. Another topic of debate has been the biexponential decay. Formosinho *et al* (1984) have argued that it is due to two states connected by reversible decay, while Marcantonatos and Deschaux (1980) have argued for an excimer theory.

The present study was undertaken in order to improve understanding of the variation of lifetime with concentration and temperature of uranyl in aqueous solution. This is important for developing a system for remote detection of uranyl in natural waters and measuring its concentration.

Table 1 shows the variation of lifetime as the concentration is changed and this is shown in figure 8, as a plot of rate parameters against concentration. The most dilute concentration at which a decay curve could be obtained, was  $2 \times 10^{-6}$  M, where the decay is seen to be only single exponential. A typical luminescence decay is shown in figure 9, which was acquired in 62 minutes. Table 2 shows the variation in the lifetime of decay as the temperature is changed at a concentration of 0.15 M, and is shown as an Arrhenius Plot in figure 10. From this figure, a negative deviation is seen to the Arrhenius Equation. However, from the residuals of figure 11, it can be seen, that the data is better described by a triple rather than a biexponential decay. The shortest lifetime is seen to fit to the Arrhenius Plot. This means that at these

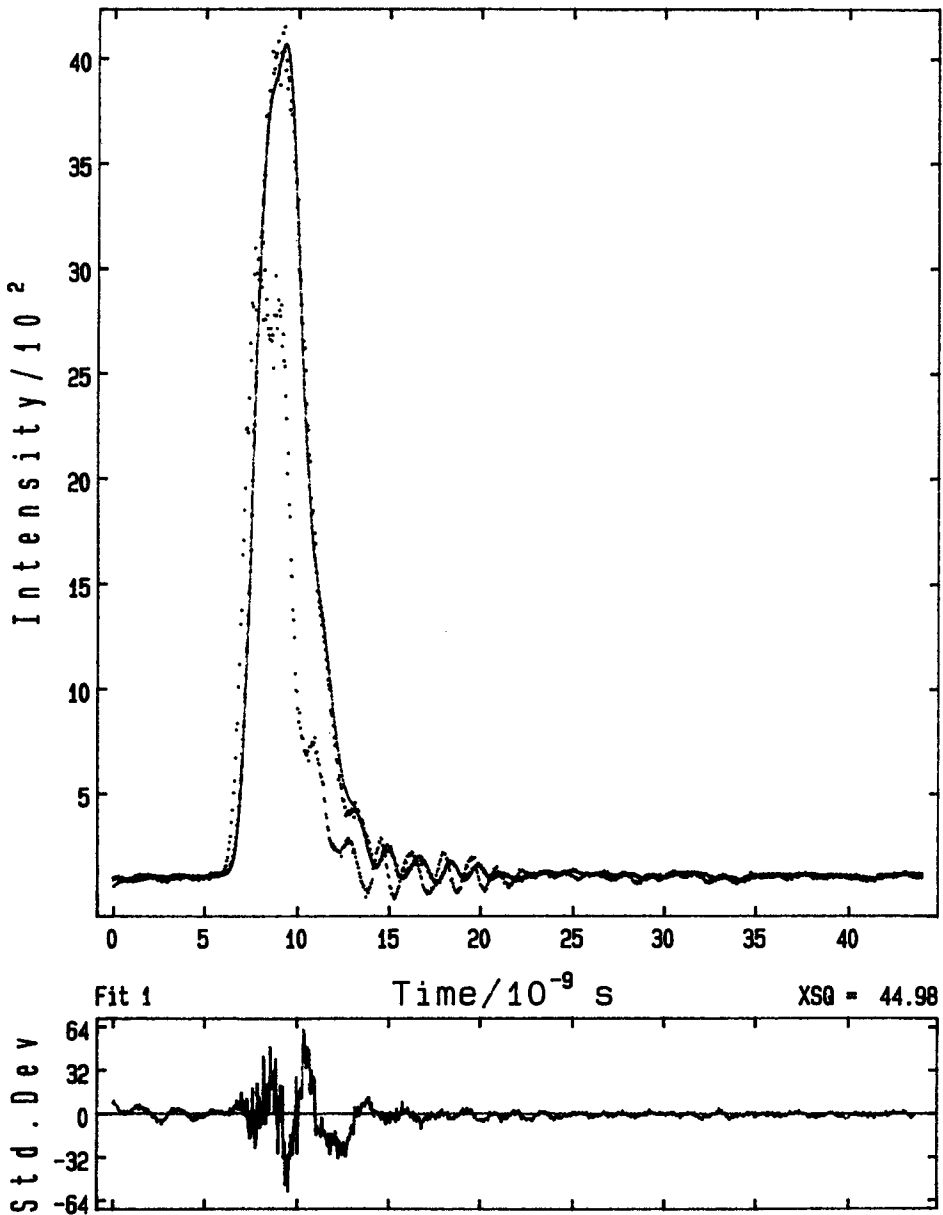


Figure 7. The nitrogen laser profile and the decay curve for rose bengal as well as the fitted function (solid line). The lifetime for rose bengal was measured as  $0.76 \pm 0.02$  ns.

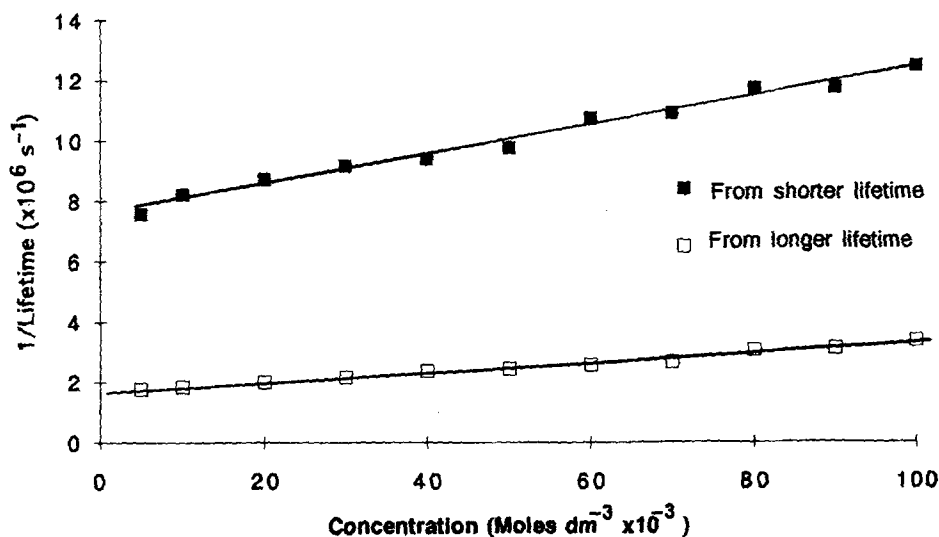
temperatures, a third emission state is present, which has a lifetime in between the two components present at normal temperatures.

### 3.3 Residuals and $\chi^2$

As can be seen from figure 6, a number of problems have yet to be fixed. The poor response from the nitrogen laser is due to the degradation of the spark gap, and is

**Table 1.** The effect of concentration on the lifetime of uranyl in triple distilled water. The data are analysed as a biexponential decay, where  $\tau$  is the lifetime, and the percentage of each component (B) is also given.

| Concentration<br>( $\times 10^{-3}$ ) M | $\tau_1$ ( $\mu$ s) | $\tau_2$ ( $\mu$ s) | $B_1$ | $B_2$ | $\chi^2$ |
|---|---------------------|---------------------|-------|-------|----------|
| 5                                       | $1.32 \pm .04$      | $5.65 \pm .02$      | 2.41  | 97.59 | 3.025    |
| 10                                      | $1.217 \pm .009$    | $5.41 \pm .001$     | 2.44  | 97.56 | 4.127    |
| 20                                      | $1.147 \pm .005$    | $4.987 \pm .003$    | 3.06  | 96.94 | 1.703    |
| 30                                      | $1.09 \pm .01$      | $4.601 \pm .005$    | 6.38  | 93.62 | 1.468    |
| 40                                      | $1.064 \pm .007$    | $4.212 \pm .004$    | 12.61 | 87.39 | 1.597    |
| 50                                      | $1.026 \pm .006$    | $4.112 \pm .005$    | 13.59 | 86.41 | 1.628    |
| 60                                      | $0.932 \pm .008$    | $3.89 \pm .01$      | 8.55  | 91.45 | 1.774    |
| 70                                      | $0.917 \pm .008$    | $3.773 \pm .009$    | 9.61  | 89.39 | 2.415    |
| 80                                      | $0.852 \pm .009$    | $3.268 \pm .004$    | 13.6  | 86.4  | 1.988    |
| 90                                      | $0.851 \pm .07$     | $3.226 \pm .006$    | 14.92 | 85.18 | 2.06     |
| 100                                     | $0.802 \pm .007$    | $2.976 \pm .003$    | 13.7  | 86.3  | 3.552    |



**Figure 8.** The rate parameters for both lifetimes ( $\tau_1$  and  $\tau_2$ ) is seen to increase linearly with increasing concentration at 32°C.

not an effect from the detector. The normalized  $\chi^2$  values, which should approach unity for a “good” fit, do not do so for these data. The fitting routines use Gaussian data weights, which assume that the noise is independent of signal amplitude. In these measurements, shot noise predominates, thus leading to too high a weighting of the signal peaks and a corresponding high value of  $\chi^2$ . With proper weighting, the  $\chi^2$  values are only meaningful in a relative sense.



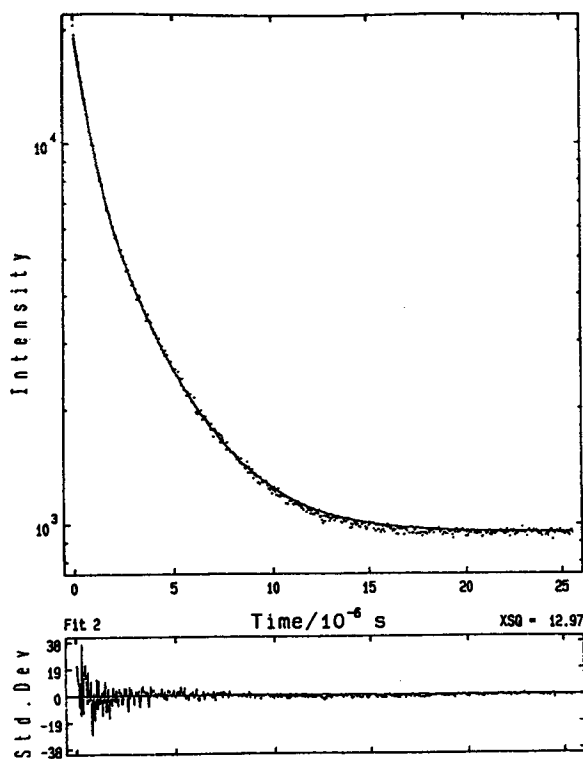
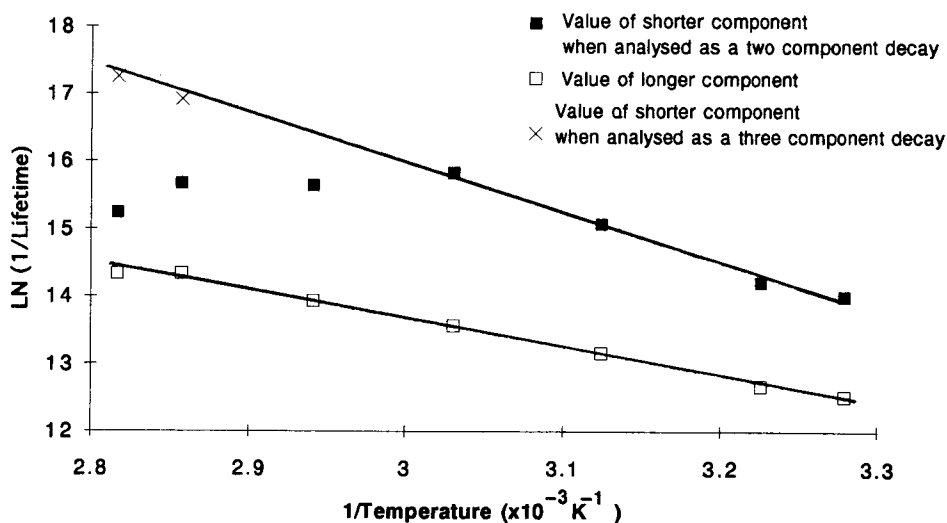


Figure 9. A typical decay curve from uranyl nitrate in aqueous solution. The concentration was 0.1 M and the data was averaged over 100 samples per point for 512 points (which took 62 min). The data was analysed as a biexponential decay and although the data fits well visually, the statistical data ( $\chi^2$ ) implies a poor fit. The fitting program expects the data to be of Poissonian Noise Distribution, but the system exhibits shot noise, and so the division of expected noise/noise in data, yields a larger value of  $\chi^2$ .

Table 2. Using an electrically heated cuvette holder, the temperature of the uranyl in aqueous solution is varied between 25 and 82°C, and the decay is analysed in terms of a biexponential decay. However, at higher temperatures, a negative deviation is seen to an Arrhenius Curve of  $K_T = A + B \exp(-\Delta E/RT)$  and the data, in some cases, can be analysed in terms of a three component decay. The data was collected over about 45 min (100 averages per data point).

| Temp.<br>(°C) | $\tau_1(\mu\text{s})$ | $\tau_2(\mu\text{s})$ | $\tau_3(\mu\text{s})$ | $B_1$ | $B_2$ | $B_3$ | $\chi^2$ |
|---------------|-----------------------|-----------------------|-----------------------|-------|-------|-------|----------|
| 32            | $0.834 \pm 0.08$      | $3.65 \pm 0.01$       |                       | 19    | 81    |       | 2.16     |
| 37            | $0.674 \pm 0.044$     | $3.152 \pm 0.01$      |                       | 11.5  | 88.5  |       | 2.77     |
| 47            | $0.285 \pm 0.001$     | $1.93 \pm 0.033$      |                       | 11    | 89    |       | 3.49     |
| 57            | $0.134 \pm 0.002$     | $1.29 \pm 0.002$      |                       | 3     | 97    |       | 3.89     |
| 67*           | $0.161 \pm 0.001$     | $0.896 \pm 0.002$     |                       | 11    | 89    |       | 4.42     |
| 77            | $0.157 \pm 0.003$     | $0.597 \pm 0.006$     |                       | 13    | 87    |       | 3.94     |
| 77            | $0.045 \pm 0.002$     | $0.615 \pm 0.006$     | $0.248 \pm 0.003$     | 1.15  | 75.91 | 22.94 | 2.69     |
| 82            | $0.241 \pm 0.006$     | $0.597 \pm 0.016$     |                       | 26    | 74    |       | 4.38     |
| 82            | $0.032 \pm 0.003$     | $0.606 \pm 0.012$     | $0.204 \pm 0.003$     | 0.4   | 56.86 | 42.7  | 3.48     |

\*A three exponential fit gave meaningless results



**Figure 10.** An Arrhenius Plot for aqueous uranyl nitrate at a concentration of 0.15 M. A negative deviation is seen for the shorter lifetime at higher temperatures, when analysed as a biexponential decay. This can be resolved if the decay is analysed as being due to a three component decay and shortest lifetime value is used.

#### 4. Conclusion

The instrument developed here has been shown to be capable of measuring lifetimes within a range of 0.75 ns to 597  $\mu\text{s}$ , and its results are in agreement with the results obtained by other workers. The use of the bifurcated fibre optic cable causes no problems from material or modal dispersion.

The success of a sampling technique depends entirely upon the response from the detector. The technique developed here for constructing dynode chains, although contrary to the popular method of keeping earth planes as far as possible from the high voltage dynode chains, was found to give superior results, if done with care, and is applicable to all types of PMTs.

The problem of incorporating correct data weighting for shot noise into the fitting routines, so that they deal with the noise distribution from data acquired on a boxcar averager (or with any averaging technique for improvement of S/N ratios) is currently being addressed.

A detailed study has been made on the effects of concentration, wavelength and temperature, but only a small portion of the work is presented here. The most interesting results have been at temperatures above 60°C, where a negative deviation to an Arrhenius Plot is seen for the shorter lifetime component. This can however be resolved, where the data is of high enough quality to be analyzed in terms of a triple exponential decay, then the shortest lifetime is seen to fit to the Arrhenius Plot.

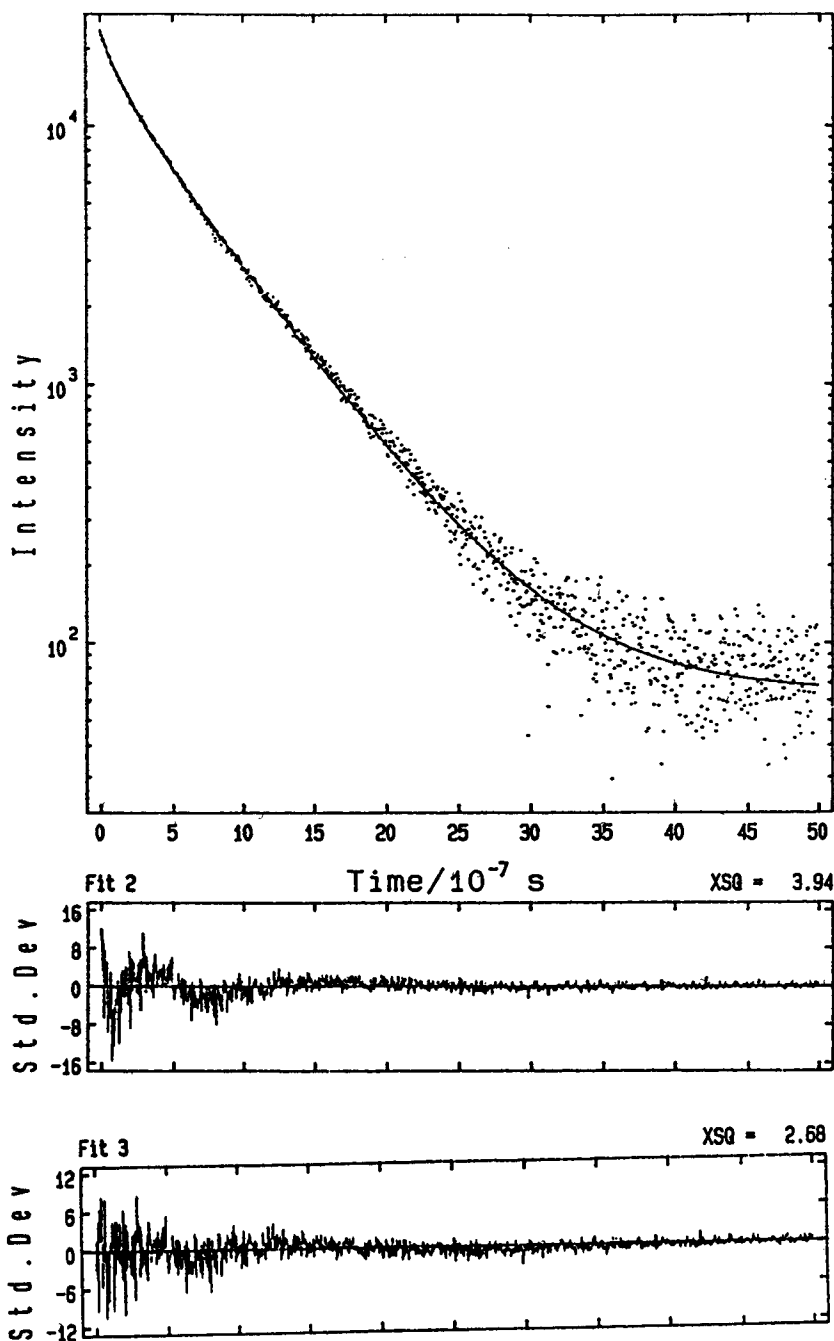


Figure 11. The decay curve for aqueous uranyl nitrate at a concentration of 0.15 M and a temperature of 82°C. From the shape of the residuals, it can be seen that the data are better described by a three-exponential decay.

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