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A BECQUEREL-DISC PHOSPHOROSCOPE FOR THE MEASUREMENT OF LIFETIMES IN ROOM-TEMPERATURE PHOSPHORIMETRY*

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Summary—A Becquerel-disc phosphoroscope is constructed from a commercially available optical chopper with variable frequency and digital read-out. By use of a continuous source, phosphorescence lifetimes in the range 1–1000 msec can be measured with better than 4% relative standard deviation.

In 1858, Becquerel reported the invention of the first phosphoroscope.[1] A phosphorescent material was mounted between two revolving discs each carrying four evenly spaced slots near the edge (and each slot has a width of $\pi/8$ radian). The discs were arranged so that light passing through a hole in the first disc and striking the sample could not be seen by looking through a hole in the second disc. A fraction of a second later, depending on the rate of revolution of the discs, the exciting light was cut off by the first disc and a hole in the second disc permitted observation of phosphorescent light emitted from the sample.[2] Becquerel's disc was capable of measuring phosphorescence with a lifetime as short as 10^{-4} sec. Later, he cemented a solid phosphor to the surface of a revolving cylinder.[3] Upon excitation at one point on the cylinder, different stages of decay were observed at different distances around the can.

Later, Wood cemented several solid phosphors to the surface of a revolving disc.[4] The lifetimes of these phosphors were estimated by observing the width of the phosphorescent band on the face of the disc. Lifetimes were reported as fractions of a revolution of the disc. More precise measurements were prevented by speed fluctuations in the driving motor and the error involved in estimating the band widths. A few years later, similar experiments were performed with a photocell detector, allowing lifetime measurements in the range 10^{-5}–5 sec.[5,6] The method was still limited by uncertainty in the measurement of the disc's angular velocity.

Recently, most measurements of phosphorescent lifetimes have been performed with pulsed excitation sources and gated detectors.[7–11] These systems are complex and more expensive but produce more precise results. The relative standard deviations (RSD) are between 2 and 10%, and the lifetimes measured vary from 0.5 to 800 msec. This communication describes a Becquerel-disc phosphoroscope which provides more precise lifetime measurements (<4% RSD) over a broad range (1–1000 msec).

THEORY

Normally, when phosphorescence lifetimes (τ_L) are determined, the phosphorescence intensity measured at some delay time (t_D) after a period of excitation and its abrupt termination is assumed to follow a simple exponential decay:

$$I_{pt} = I_{po} \exp(-t_D/\tau_L) \quad (1)$$

where I_{po} is the phosphorescence intensity which would be measured if the excitation period was long enough to allow it to reach a steady-state value and I_{pt} is the intensity at time t_D. It is assumed that the exposure time (t_E) and the time between successive exposures (t_C) remain constant for measurements of I_{pt} at different delay times. Figure 1 is a graphical representation of two cycles of excitation with subsequent phosphorescence decay.

An equation for the phosphorescence intensity which accounts for the excitation and measurement processes was reported by O'Haver and Winefordner[12] and is

$$I_{pt} = I_{po} \exp(-t_D/\tau_L) \frac{[1 - \exp(-t_E/\tau_L)]}{[1 - \exp(-t_C/\tau_L)]} \quad (2)$$

This equation accounts for the diminished phosphorescence intensity growth when a shorter exposure time, t_E, is used for a particular measurement of I_{pt}. It also accounts for changes in the phosphorescence intensity, prior to exposure, due to changes in time between exposures, t_C. For lifetimes measured with a variable-speed phosphoroscope, equation (2) must be considered. If a pulsed-source system is employed equation (1) is suitable, since the pulse width (t_E) and the source-repetition rate ($1/t_C$) may be held constant, while the delay time may be

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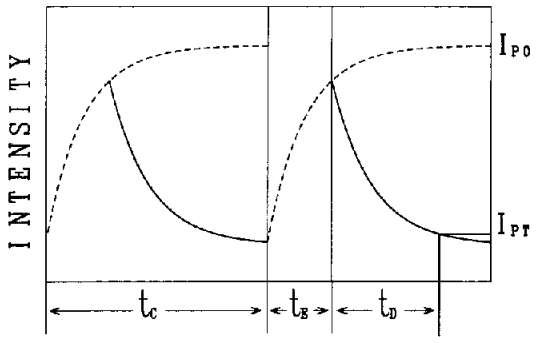

Fig. 1. Graphical representation of the operation of a Becquerel-disc phosphoroscope.

varied by changing the delay time on a gated detector, or by viewing the entire signal *vs.* time trace directly from an oscilloscope.

In the particular case of a rotating-disc phosphoroscope with a phosphor covering the entire front surface of the disc, some simplifications can be made for equation (2). The times t_C, t_E and t_D are determined by the angular velocity of the disc. Expressions for t_E and t_C may be found in terms of t_D and then substituted into equation (2). In our case, with a 1-inch disc, excitation of the phosphor occurs at a single point near the edge of the disc, producing a ring of phosphorescence 25 mm in diameter (Fig. 2). For a given angular velocity, the time between exposures corresponds to the distance between successive exposures, *i.e.* to the length of the phosphorescent ring (80 mm). The exposure time corresponds to the size of the excitation beam (1 mm) focused onto the surface of the disc. Phosphorescence is collected at a point 90° away from the excitation point in the direction of the rotation, so t_D corresponds to 1/4 revolution of the disc, or a 20-mm length of the phosphorescent ring. Taking these factors into account results in the decay expression

$$I_{pt} = I_{po} \exp(-t_D/\tau_L) \frac{[1-\exp(-t_D/20\tau_L)]}{[1-\exp(-4t_D/\tau_L)]} \quad (3)$$

Further reduction of equation (3) is difficult. At this point, it it useful to compare some hypothetical results for lifetimes calculated by equation (3), with those calculated by using equation (1). With equation (1), the phosphorescence lifetime is determined by taking the inverse of the slope of a plot of $\ln(I_{pt})$ *vs.* t_D where:

$$\ln(I_{pt}) = \ln(I_{po}) - \frac{t_D}{\tau_L} \quad (4)$$

Equation (4) can be rearranged to show that a plot of $\ln(I_{pt}/I_{po})$ *vs.* t_D/τ_L will be linear, with a slope of -1. By assuming values for t_D/τ_L, values for I_{pt}/I_{po} can be calculated by using equation (3). A plot of $\ln(I_{pt}/I_{po})$ *vs.* t_D/τ_L is found to be a curve with a maximum at $t_D/\tau_L \sim 1$, and approaching linearity with a slope of -1 at $t_D/\tau_L > 5$ (Fig. 3). Unfortunately, at $t_D/\tau_L > 5$, the phosphorescence intensity of most samples is too weak to measure. On the other hand, measurements are easily made in the region $1 < t_D/\tau_L < 3$, where the average slope of the curve is -0.54. This implies that a phosphorescence lifetime (τ_L^m) measured by using equation (4) for a variable-speed rotating disc phosphoroscope must be multiplied by a factor of 0.54 to obtain the correct luminescence lifetime τ_L

$$\tau_L^c = 0.54\,\tau_L^m \quad (5)$$

The factor relating τ_L^c to τ_L^m is independent of τ_L^m as long as that portion of the plot is used where $\tau_L^m < t_D < 3\tau_L^m$. This region is easily located experimentally without previous knowledge of τ_L^m, by beginning measurements at a delay time corresponding to the peak phosphorescence intensity and continuing to a delay time three times as large.

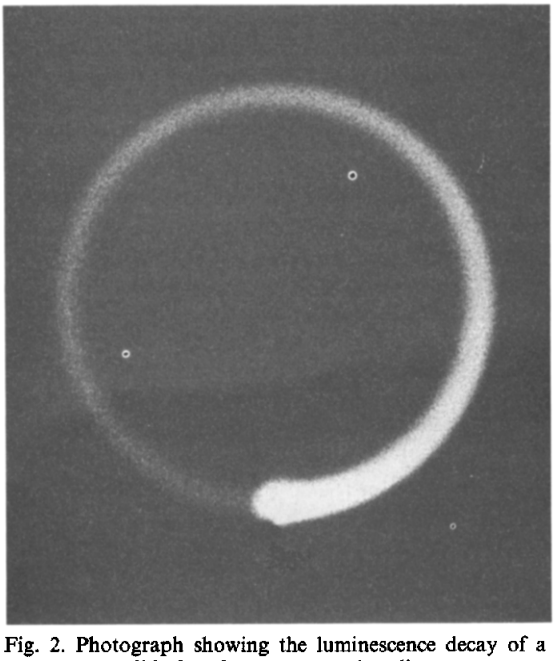

Fig. 2. Photograph showing the luminescence decay of a solid phosphor on a rotating disc.

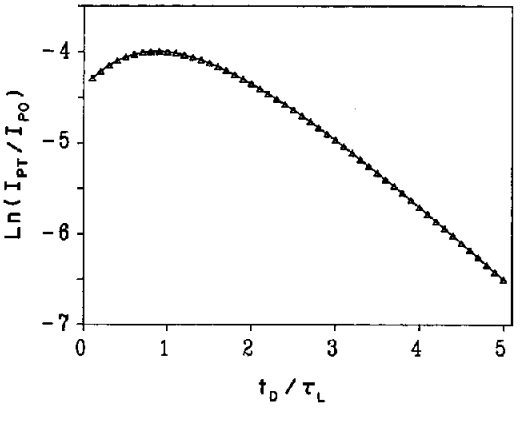

Fig. 3. Theoretical plot of the natural logarithm of relative phosphorescence intensity *vs.* relative delay time as calculated by using equation (3).

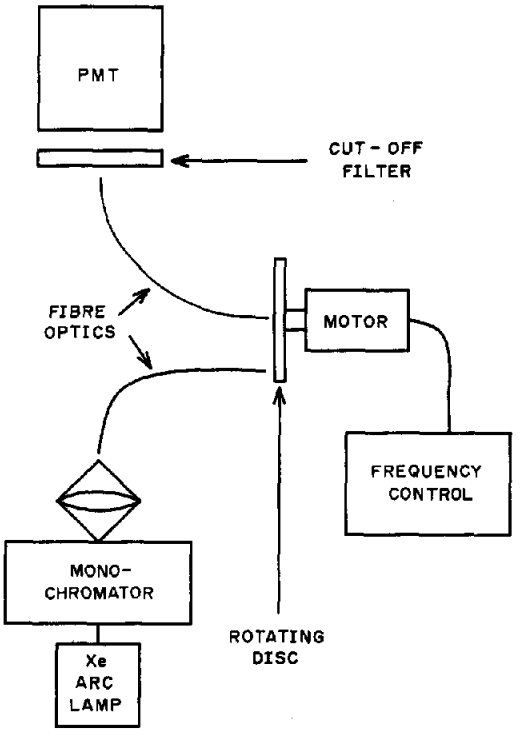

Fig. 4. Instrumental arrangement used to measure lifetimes with a Becquerel-disc phosphoroscope. As stated in the text, the two fibre optics are positioned 5 mm in from the edge of the disc, at 90° and 180° from top dead centre.

EXPERIMENTAL

A diagram showing the instrumental arrangement for the Becquerel-disc phosphoroscope is given in Fig. 4. The excitation source was a 150-W xenon arc lamp (Varian Assoc., Palo Alto, CA). Source radiation was passed through a 0.1-m monochromator (ISA, Metuchen, NJ). A 16-nm band of radiant flux leaving the exit slit of the monochromator was focused into a fibre optic with a microscope objective. The exit end of the fibre optic was placed 2 mm away from the surface of the rotating disc carrying the sample. The fibre optic was positioned opposite the bottom centre of the disc, 5 mm from the edge. The excitation beam covered a 1-mm diameter circle on the disc surface. Phosphorescence from the sample was collected by a second fibre optic opposite a point 5 mm in from the right-hand side of the disc, at the upper edge of the quadrant starting from the excitation point. The exit end of the emission fibre optic was coupled to a cooled photomultiplier tube (EMI Model 9789, Plainview, NY). A coloured glass cut-off filter blocking light of wavelength shorter than 450 nm was positioned between the fibre optic and the photomultiplier tube (PMT). The signal from the PMT was recorded directly on a strip-chart recorder (Houston Instruments, Austin, TX).

The rotating-disc phosphorescence consisted of a commercially available optical chopper with a 35-mm diameter aluminium disc. The chopper used was the Model OC 4000 (Photon Technology, Inc., Princeton, NJ) and could turn the disc at variable rates between 0.133 and 133 Hz. The frequency was recorded manually from a six-digit LED display on the controller. The aluminium disc was home-built and easily removable for sample application.

The lifetimes of several phosphorescent species were measured to demonstrate the useful range of the phosphoroscope. Three solid phosphors were obtained from the National Bureau of Standards. They were: standard reference material (SRM) No. 1023—a zinc cadmium sulphide phosphor with silver as activator, SRM No. 1028—a zinc silicate phosphor with manganese as activator and SRM No. 1030—a magnesium arsenate phosphor with manganese as activator. About 0.1 g of each phosphor was applied to the surface of the rotating disc with 0.5 ml of clear optical cement. The mixture was spread evenly so that it covered the entire face of the disc.

Three molecular samples known to produce room-temperature phosphorescence when adsorbed on filter paper were also tested. Pyrene, quinine, and fluoranthene (Aldrich, Milwaukee, WI) were dissolved in absolute ethanol (1 mg/ml); a 250-μl portion of sample solution was spotted onto 1-inch discs of filter paper (Schleicher and Schüll 593-C) previously treated with 250 μl off 0.5M lead acetate. The filter paper was allowed to dry in air for 15 min before being glued to the rotating disc.

Finally, a "glow in the dark" phosphorescent paint was applied to the disc. The yellow paint was purchased at a local hobby store and was used to demonstrate that the phosphoroscope was capable of measuring lifetimes of the order of 1 sec. The paint was applied directly to the disc and allowed to dry for 15 min.

The measurement process was as follows. After a sample had been applied to the disc, a range of disc speeds was selected. The speeds corresponded to delay times of 2–2000 msec between excitation and observation of phosphorescence. The signal for each delay time was recorded and a plot of signal *vs.* t_D was generated (Fig. 5). Each plot was fitted with a simple exponential decay function [equation (1)]. The linear region of a plot of $\ln(I_{pt})$ *vs.* t_D had a slope equal to $-1/\tau_L^m$ where τ_L^m was the measured lifetime of the luminescence. The actual phosphorescence lifetime, τ_L^c, was calculated by using equation (5). The precision of the τ_L^c measurements was calculated by finding the standard deviation of the slope of the line.

Lifetimes determined with the Becquerel-disc phosphoroscope were compared with those determined by using a pulsed-source system. The instrumental arrangement used for the pulsed-source measurements was constructed from parts obtained commercially. The excitation source was a 300-W xenon arc flashlamp (Xenon Corp, Wilmington, MA). Source radiation was passed through a 0.33-m monochromator (GCA/McPherson, Acton, MA) onto the sample. Phosphorescence was collected through a similar monochromator with a photomultiplier tube attachment. The signal from the PMT was amplified and directed to a digital storage oscilloscope (Tektronix Model 2430A, Beaverton, Oregon). A decay curve averaged over 256 excitation pulses was stored. Data points (t_D, I_{pt}), were read directly from the oscilloscope display. Lifetimes were calcu-

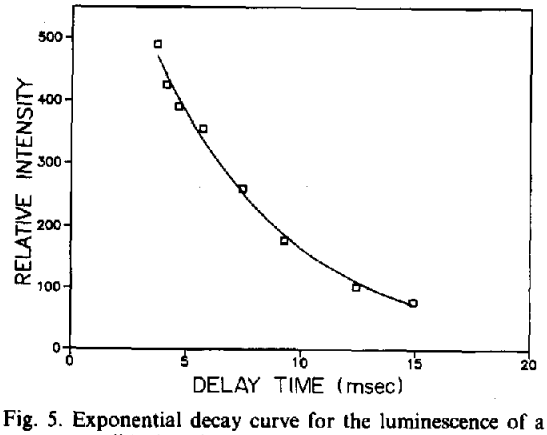

Fig. 5. Exponential decay curve for the luminescence of a solid phosphor (NBS SRM No. 1030).

Table 1. Phosphorescence lifetimes measured with a Becquerel-disc phosphoroscope

Phosphor	System*	λ_{ex}, *nm*	λ_{em}, *nm*	Lifetime,† *msec*	RSD, %	Correlation‡ coefficient
SRM No. 1023	A	380	Yellow	3.1 ± 0.2	2.1	0.9983
	B	380	590	3.7 ± 1.5	8.4	0.9695
SRM No. 1028	A	375	Yellow/Green	2.3 ± 0.1	1.3	0.9987
	B	375	540	2.7 ± 0.2	2.5	0.9952
SRM No. 1030	A	420	Red	3.2 ± 0.4	3.2	0.9971
	B	420	695	2.8 ± 0.2	1.9	0.9989
Fluoranthene	A	365	Yellow/Green	11.1 ± 0.8	2.1	0.9981
	B	365	545	14.3 ± 5.5	8.2	0.9733
Pyrene	A	340	Orange	9.9 ± 0.9	2.5	0.9972
	B	340	595	7.7 ± 1.1	3.9	0.9925
Quinine	A	335	Green	22.0 ± 1.4	1.8	0.9987
	B	335	510	25 ± 15	16.3	0.9944
Phosphorescent§ paint	A	400	Yellow	813 ± 10	1.3	0.9993
	B	400	570	—	—	—

*System A is the Becquerel-disc phosphoroscope; System B is a pulsed-source system.
†Lifetimes are reported along with 99% confidence limits.
‡Correlation coefficients are reported for a linear plot of delay time *vs.* ln(signal).
§The lifetime of the phosphorescent paint could not be measured with the pulsed-source system.

lated from a plot of equation (4). The same number of data points, with the same delay times, were used for both pulsed-source and Becquerel-disc measurements.

RESULTS AND DISCUSSION

A photograph of the phosphorescence decay of NBS SRM No. 1023 is shown in Fig. 2. Excitation light from the fibre optic strikes the sample at the bottom of the rotating disc as it moves in an anti-clockwise direction. The decaying phosphorescence can be seen along the periphery of the disc. The "emission" (collection) fibre optic has been removed from the photo for clarity.

Table 1 gives the lifetimes measured for seven phosphors by the two methods. The good agreement between the two methods suggests that the assumptions made in the derivation of equation (5) are valid. The precision (relative standard deviation) is better by a factor of ~2 for the Becquerel-disc measurements. The Becquerel-disc phosphoroscope is also capable of measuring longer lifetimes than the flashlamp system can. This is a result of the fixed pulse-rate of the flashlamp, 4 Hz, which restricts lifetime measurements to below 250 msec.

The Becquerel-disc phosphoroscope is ideally suited to the measurement of lifetimes of phosphorescence analytes on solid substrates; such information is not readily available in the literature. A few lifetimes have been reported for several indoles,[10] and for several organic acids[7] absorbed on filter paper, but no extensive tables of lifetimes covering a wide range of compounds have been published. The Becquerel-disc phosphoroscope described here could be used to generate such data easily and reliably. Such an endeavour would benefit those interested in the analysis of complex mixtures by time-resolved phosphorimetry.

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REFERENCES

1. E. Becquerel, *Ann. Chim. Phys.*, 1859, **55**, 1 (see p. 79 and Plate II).
2. E. N. Harvey, *A History of Luminescence*, p. 349. American Philosophical Society, Philadelphia, 1957.
3. E. Becquerel, *Ann. Chim. Phys.*, 1861, **62**, 5 (see p. 10 and Plate I).
4. R. W. Wood, *Proc. Roy. Soc. London*, 1921, **A99**, 362.
5. V. W. Bünger and W. Flechsig, *Z. Phys.*, 1931, **67**, 42.
6. P. Pringsheim and M. Vogel, *Luminescence of Liquids and Solids*, p. 63. Interscience, New York, 1943.
7. E. M. Schulman and C. Walling, *J. Phys. Chem.*, 1973, **77**, 902.
8. D. E. Goering and H. L. Pardue, *Anal. Chem.*, 1979, **51**, 1054.
9. G. Scharf and J. D. Winefordner, *Talanta*, 1986, **33**, 17.
10. J. J. Aaron, M. Andino and J. D. Winefordner, *Anal. Chim. Acta*, 1984, **160**, 171.
11. G. Scharf and J. D. Winefordner, *Spectrochim. Acta*, 1985, **41A**, 899.
12. T. C. O'Haver and J. D. Winefordner, *Anal. Chem.*, 1988, **38**, 602.