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Application News

No.A493

Spectrophotometric Analysis

Measuring Peroxyoxalate Chemiluminescence Using a Spectrofluorophotometer

Chemiluminescence is a phenomenon where molecules are excited by a chemical reaction and then emit light energy as they return to ground state. Chemiluminescence based on using oxalate esters features high-emission efficiency and long emission time and provides illumination for long periods without any electricity. Consequently, it is used for recreational, fishing, and many other applications where it is commonly called glow sticks. The following describes the luminescent process of peroxyoxalate chemiluminescence and gives an example of using an RF-6000 spectrofluorophotometer to measure the emission spectra of glow sticks.

Luminescent Process of Peroxyoxalate Chemiluminescence

Peroxyoxalate chemiluminescence is caused by a chemical reaction between an oxalate ester and hydrogen peroxide within a fluorescent dye solution. As shown in Fig. 1, the oxalate ester is oxidized by hydrogen peroxide to produce ROH and 1,2-dioxetanedione. The 1,2-dioxetanedione is a high-energy reaction intermediate that exchanges electrons with the fluorescent dye as it breaks down to carbon dioxide. However, when the electrons return to the fluorescent dye, they enter the lowest unoccupied molecular orbital, causing the fluorescent dye to be in an excited state.[1), 2)] Then the excited fluorescent dye releases light (hv) when it returns to its ground state, where the wavelength of that light depends on the fluorescent dye.

Fluorescent Dyes Used in Glow Sticks

Commercially marketed glow sticks are shown in Fig. 2. The oxalate ester and fluorescent dye solution are placed in a sealed thin-walled glass container and the glass container is placed inside a polyethylene tube together with hydrogen peroxide solution to which a catalyst is added. Bending the polyethylene tube breaks the glass container, which causes both solutions to mix together and emit light.

Examples of the fluorescent dyes used in glow sticks are shown in Fig. 3. Polycyclic aromatic fluorescent dyes are used, which emit different colors based on the wavelength of light emitted when the fluorescent dyes change from excited to ground state.

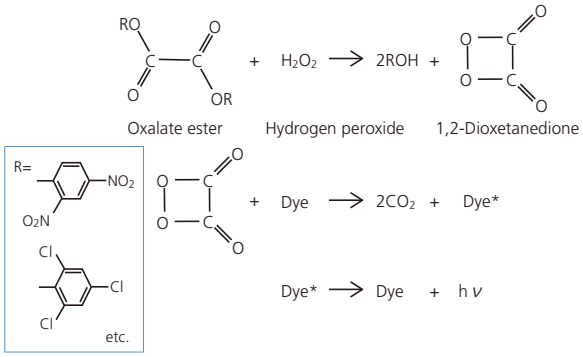

Fig. 1 Luminescent Process of Peroxyoxalate Chemiluminescence

Fig. 2 Glow Sticks

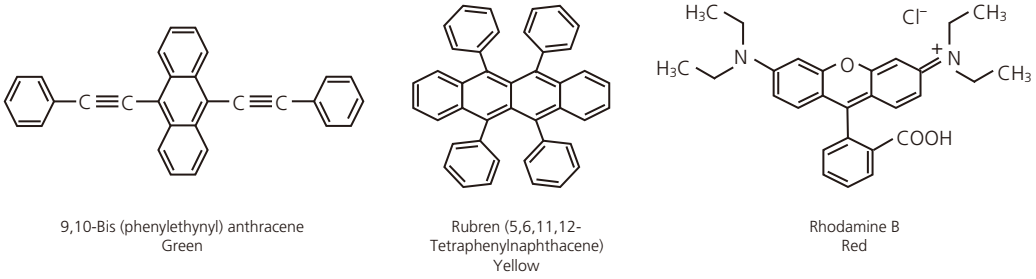

Fig. 3 Fluorescent Dyes Used in Glow Sticks

Measuring the Light Emitted From Glow Sticks

A diagram of the RF-6000 spectrofluorophotometer system and its sample compartment is shown in Fig. 4. A shutter placed in front of the excitation light inlet window was closed to prevent excitation light from entering the sample compartment. A metal mesh filter was placed next to the fluorescent light outlet to reduce the amount of light reaching the detector.
The small lid inside the sample compartment cover was removed to insert the glow sticks into the sample compartment. Additionally, a blackout curtain was placed over the glow stick to prevent external light from entering the sample compartment.
Fig. 5 shows the corresponding emission spectra of yellow-green, yellow, and red glow sticks. Measurement conditions are indicated in Table 1.

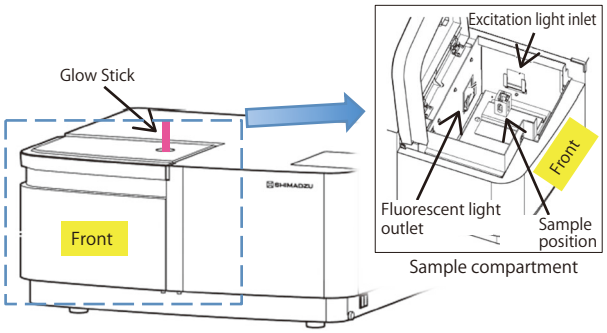

Fig. 4 Diagram of RF-6000 Spectrofluorophotometer and Sample Compartment

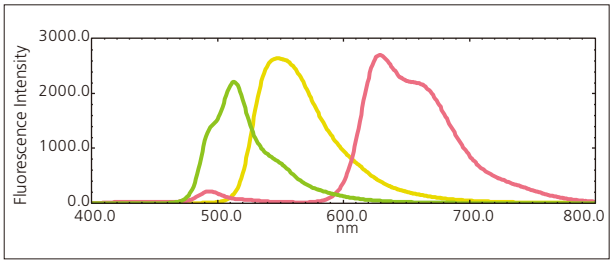

Fig. 5 Emission Spectra of Glow Sticks
The color of spectrum corresponds to the glow stick color.

Table 1 Instrument and Analytical Conditions

Instrument	: RF-6000 spectrofluorophotometer
Fluorescent light measurement wavelength range	: 400 to 800 nm
Scan speed	: 60 nm/min
Sampling interval	: 1 nm
Fluorescent light band width	: 3 nm
Sensitivity	: Low

Time-Course Measurement of Glow Sticks

The red glow stick was bent, placed in the RF-6000 sample compartment, and its emission spectrum was measured as a function of time for 100 minutes. Measurement results are shown in Fig. 6 and measurement conditions in Table 2. Due to the active chemical reaction and correspondingly high level of fluorescent dye excitation, the brightness was high immediately after bending the glow stick, but the initial brightness quickly diminished. The results show that about 10 minutes later, the reaction slowed and brightness decreased at a roughly constant rate.

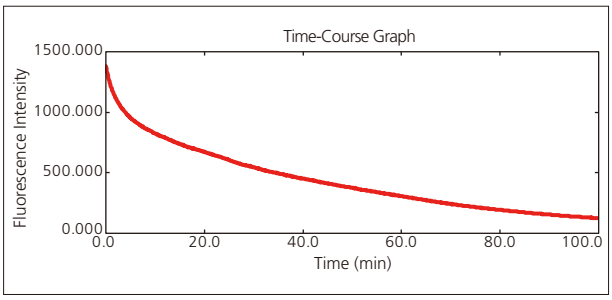

Fig. 6 Time-Course Measurement of Red Glow Stick

Conclusion

An RF-6000 spectrofluorophotometer was used to measure the light emitted from glow sticks based on peroxyoxalate chemiluminescence. The RF-6000 is able to measure wavelengths from 200 nm to 900 nm, which was especially helpful for investigating light emission phenomena over a wide range of wavelengths.

Table 2 Instrument and Analytical Conditions

Instrument	: RF-6000 spectrofluorophotometer
Fluorescence wavelength	: 629 nm
Data interval	: 0.1 min
Fluorescent light band width	: 3 nm
Integration time	: 500 ms
Sensitivity	: Low

[References]
1) C. V. Stevani, S. M. Silva, W. J. Baader, *Eur. J. Org. Chem*., 4037 (2000)
2) S.Ohba, T. Mukai, Hiyoshi Review of Natural Science Keio University No.49, 1 (2011)

First Edition: Oct. 2015

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