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Application News

No. A561

Spectrophotometric Analysis

Light Emission Measurement at Low Temperature - Utilizing the Low-temperature Measurement Unit -

Light emission such as fluorescence occurs at transitions from the excited state to the ground state. The efficiency (η) of such emissions is expressed by the following equation based on the ratio of radiative transitions (W_R) and non-radiative transitions (W_{NR}).

$$\eta = W_R / (W_R + W_{NR})$$

Transitions from the excited state are greatly affected by the surrounding environment and heat has a substantial influence on emissions. Greater influences from heat increase non-radiative transitions, which in turn lowers emission efficiency and results in lower emission intensities. Therefore, to avoid the influence of heat, many measurements are done by lowering the sample temperature such as by using liquid nitrogen.

This article introduces measurements of liquid and powder samples cooled down to liquid nitrogen temperature (77 K) using a low-temperature measurement unit[*1] combined with the RF-6000 spectrofluorophotometer.

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Low-temperature Measurement of Liquid

Fig. 1 shows a cross-section of the low-temperature measurement unit. The low-temperature measurement unit holds a Dewar vessel in the sample chamber. The vessel is filled with liquid nitrogen and by setting a sample rod containing the sample in the vessel, the sample is cooled down to about liquid nitrogen temperature (77 K). As shown in Fig. 2, an observation window is designed on the front side of the sample chamber for sample observation, allowing operators to visually check if the sample is being irradiated with excitation light, or if the sample is emitting light.

Figs. 3 and Figs. 4 show the results of measuring naphthalene solutions (solvent: ethanol) with two differing concentrations (1.0×10^{-5} mol/L and 5.0×10^{-5} mol/L) at room temperature (300 K) and at liquid nitrogen temperature (77 K). The measurement conditions are listed in Table 1.

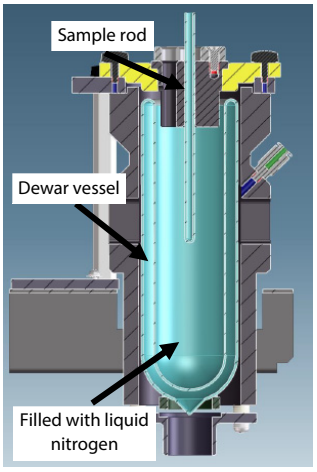

Fig. 1 Cross-section of the Low-temperature Measurement Unit

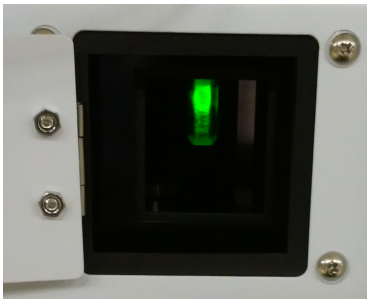

Fig. 2 The Sample Chamber from the Observation Window (Excitation light irradiated)

Table 1 Measurement Conditions

Instrument	: RF-6000, low-temperature measurement unit
Excitation Wavelength	: 275 nm
Measurement Wavelength Range	: 290 nm to 530 nm
Scan Speed	: 200 nm/min
Data Interval	: 1.0 nm
Bandwidth	: Ex 3.0 nm, Em 5.0 nm
Sensitivity	: Low

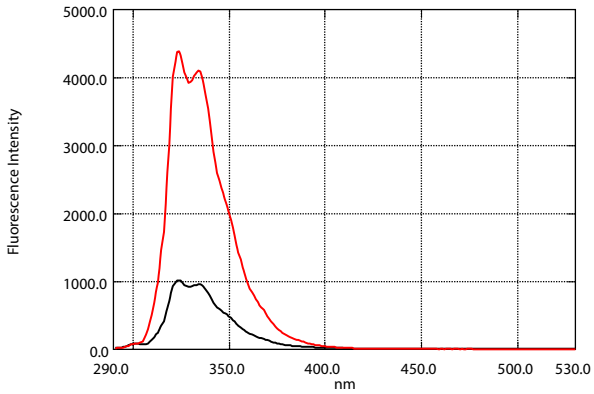

Fig. 3 Spectra at Room Temperature (300 K) Black: 1.0×10^{-5} mol/L, Red: 5.0×10^{-5} mol/L

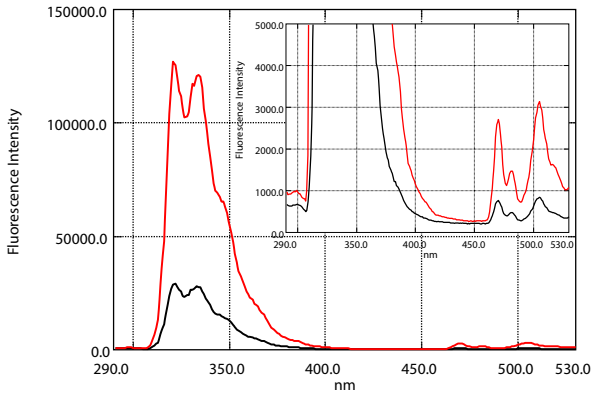

Fig. 4 Spectra at Liquid Nitrogen Temperature (77 K) Black: 1.0×10^{-5} mol/L, Red: 5.0×10^{-5} mol/L

Since the emission efficiency increased with the measurement at low temperature, signals were detected in the long-wavelength range near 500 nm in addition to the peaks near 325 nm and 335 nm which were observed at room temperature.

Fig. 5 shows the view from the observation window of the sample being irradiated with excitation light and the same view about one second after closing the shutter. Emission with a long lifetime (phosphorescence) can also be observed.

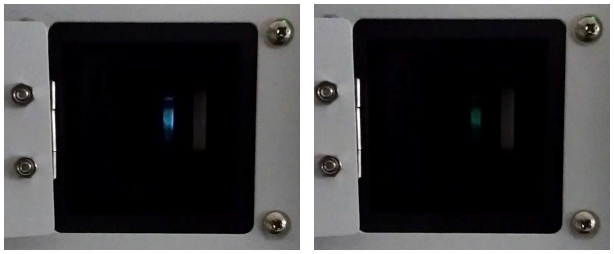

Fig. 5 Left: With Excitation Light Irradiation, Right: About One Second after Closing the Shutter

Low-temperature Measurement of Powder

Fig. 6 shows a sample rod for low-temperature measurement of powder or minute amounts of liquid. Composed of three acrylic plates, the sample is filled in a space 1-mm thick. The sample is cooled by immersing the projection on the right side of the rod (shown in Fig. 6) in liquid nitrogen, thereby allowing low-temperature measurement.

Fig. 7 shows the results of measuring benzophenone powder at room temperature (300 K) and at liquid nitrogen temperature (77 K). The measurement conditions are listed in Table 2.

Compared to room temperature, the low-temperature measurement yielded more sharp signals. This can expected to be because whereas there is an energy deactivation process relating to heat at room temperature, the process decreases at low temperature.

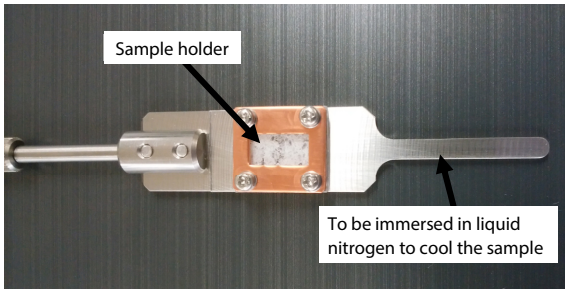

Fig. 6 Sample Rod for Powder or Minute Amounts of Liquid

Table 2 Measurement Conditions

Instrument	: RF-6000, low-temperature measurement unit
Excitation Wavelength	: 350 nm
Measurement Wavelength Range	: 370 nm to 660 nm
Scan Speed	: 200 nm/min
Data Interval	: 1.0 nm
Bandwidth	: Ex 3.0 nm, Em 5.0 nm
Sensitivity	: Low

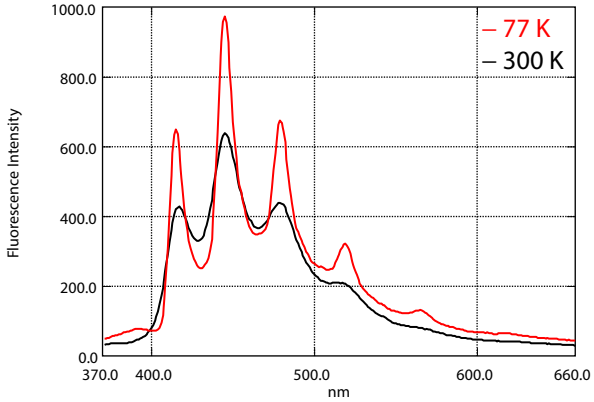

Fig. 7 Spectra of Benzophenone Powder Black: Room Temperature (300 K), Red: Liquid Nitrogen Temperature (77 K)

Conclusion

The light emission properties of liquid and powder at low temperature were successfully examined using the RF-6000 spectrofluorophotometer and low-temperature measurement unit.

With naphthalene solutions (solvent: ethanol), emissions which could not be observed at room temperature appeared in the spectra and also were observed visually from the observation window of the low-temperature measurement unit. Regarding the low-temperature measurement of benzophenone powder, sharper signals were obtained compared to the room temperature spectrum.

Reference
Organized and edited by the Phosphor Research Society: Phosphor Handbook (Ohmsha, Ltd.) (in Japanese)

*1 This unit is a semi-custom made product. Please contact Shimadzu for further details.

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