

A study of quantum efficiency measurement for phosphor solutions

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Recent times have seen an increase in the development of fluorescent and phosphorescent materials for applications including LED lamps and EL. We have reported on the development of a quantum efficiency measurement system for powder samples [1]. The main issue has been to measure quantum efficiency to evaluate it for solution samples. In this study, we have developed measurement process for quantum efficiency using integrating hemisphere system with eliminating the problem of 2nd order fluorescence, which is called "Re-excitation". We have used our system to perform measurements on Fluorescein ($C_{20}H_{12}O_5$, MW: 332.306) and Quinine Sulfate, dihydrate ($C_{20}H_{24}N_2O_2$, MW: 782.96) and some other materials as standard samples. The results, which we report here, correspond to the literature values [2-5].

Keywords: LED, Phosphor, Quantum efficiency, Integrating sphere, Integrating hemisphere.

Introduction

It is a big theme in recent times to evaluate the performance of phosphors used in illuminating light sources and display devices with LEDs and/or ELs as they develop and proliferate. In particular, for one of the important evaluation parameters, quantum efficiency, we proposed a measurement method for fluorescent powder samples using an integrating sphere traceable to the light bulb of the spectral irradiance standard supplied by JCSS (Japan Calibration Service System) [1]. However, a frequent request these days is to evaluate not only powder samples but also solution samples. So, a measurement system using an integrating hemisphere capable of flexibly handling samples in any forms was constructed. This system comprises a 150 W xenon lamp, a monochromator to the specified excitation wavelength, an integrating hemisphere to measure excitation and fluorescent light at the same time and a spectrometer (MCPD-9800). This system also can eliminate "re-excitation" fluorescence (details are described below) to get the actual quantum efficiency values. We consider and report on our discussion of a method to measure phosphor solution samples by utilizing this system and on our verification of the system by evaluating standard phosphor materials.

Experiments

Principles of quantum efficiency measurement

The external quantum efficiency of phosphor is the ratio of the number of photons of fluorescent emission

generated to that of the excitation light irradiated on the fluorescent material. On the other hand, the internal quantum efficiency of phosphor is the ratio of the number of photons of fluorescent emission to that of the excitation light absorbed by the phosphor. The latter is calculated by subtracting the number of photons of the component not absorbed but transmitted from the phosphor solution from that of the fluorescent light irradiated on the phosphor.

Taking the spectra of the excitation light irradiated on the phosphor, the transmitted light, and the fluorescent light as $E(\lambda)$, $T(\lambda)$, and $P(\lambda)$ respectively, the external and internal quantum efficiencies, ϕ_E and ϕ_I , are expressed by the equation given below. Here, the number of photons is calculated by dividing the irradiation energy by the energy hc/λ per photon with wavelength λ (h = Planck constant, and c = speed of light). The term hc is cancelled out, being present in both the numerator and the denominator.

$$\text{Quantum Efficiency (External)} \quad \Phi_E = \frac{\int_{\lambda_2}^{\lambda_4} \lambda \cdot P(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_4} \lambda \cdot E(\lambda) d\lambda} \quad (1)$$

$$\text{Quantum Efficiency (Internal)} \quad \Phi_I = \frac{\int_{\lambda_2}^{\lambda_4} \lambda \cdot P(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_4} \lambda \cdot \{E(\lambda) - T(\lambda)\} d\lambda} \quad (2)$$

Equations (1) and (2) make it possible to calculate the quantum efficiency, ϕ , by relative spectral distribution measurement because the device constants present in

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both the numerator and the denominator are cancelled out, by measuring $E(\lambda)$, $T(\lambda)$, and $P(\lambda)$ using a spectral photo detector equipped within the same optical system.

System configuration

Fig. 1 shows the Quantum Efficiency Measurement System; QE-1100, optical system of the measurement system we developed at this time. It is divided roughly into four parts: The excitation light source, integrating hemisphere, spectral photometer, and data processing unit.

The excitation light source was configured as a combination of a xenon lamp (Hamamatsu Photonics' E7536: 150 W, ozone-free) and a grating spectrometer (Shimadzu's SPG-120UV). This part can generate an excitation beam of monochromatic light with a wavelength range of 250 - 700 nm.

The integrating hemisphere is a Labsphere product with a diameter of 150 mm, and the inner wall is made of Spectralon® with a reflectance of 95% or more. The ceiling of the integrating hemisphere is made of aluminum mirror with high reflectance through UV to Visible region. The solution sample was inserted through a hole in the center of the top plate and held suspended within the integrating hemisphere. The same optical system captured the excitation light, the diffusive light that is the fluorescent light emitted by the phosphor's solution, and the transmitted light that is the excitation light transmitted from that solution. A polychromator, which is a spectral photo detector, measured the spectra.

The spectral photo detector was Otsuka Electronics' MCPD-9800. This device guides the light to the incident slit of the polychromator through a light fiber probe made of quartz, and a CCD array of the backplane irradiation type receives the light dispersed by the grating.

The measurement system with MCPD-9800 is calibrated by a standard light bulb traceable to NIST (National Institute of Standards and Technology). This makes it possible to calculate quantum efficiency based on the spectrum obtained by this system.

How to measure quantum efficiency

Here, we will describe how to measure quantum efficiency using integrating hemisphere system. As shown in the previous paper [1], "re-excitation" problem always occurs as long as the integrating sphere system is used. "Re-excitation" problem is defined as follows;

- Excitation light reflected or transmitted by a phosphor sample is diffuse-reflected on the internal wall of the sphere.
- The excitation light reflected on the sphere wall goes to the sample again.
- And it results extra fluorescence.

Thus the measured intensity includes both the actual fluorescent intensity and the re-excitation fluorescence. It is important to eliminate "re-excitation" from measured value.

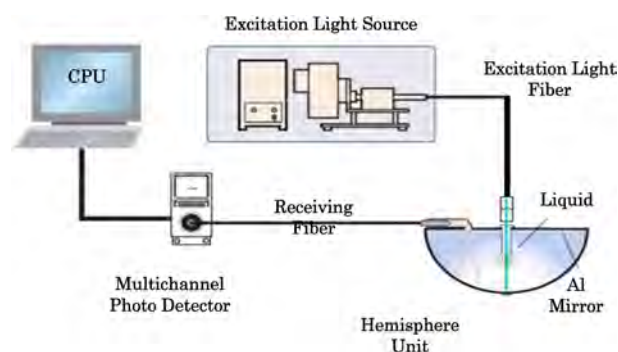


Fig. 1. System configuration of quantum efficiency measurement system.

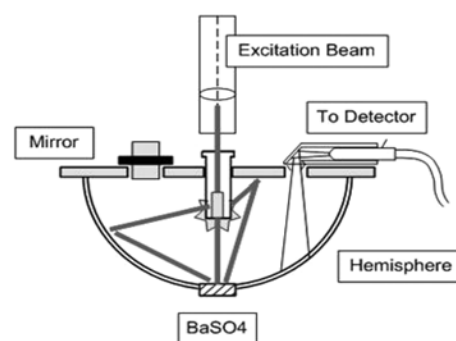


Fig. 2. Integrating hemisphere structure and a sample setting.

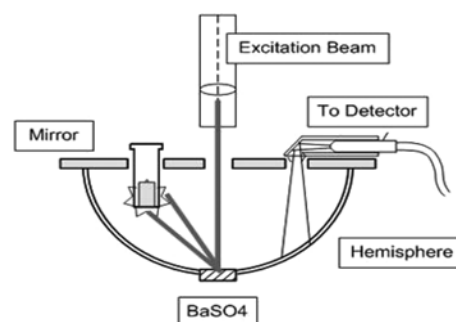


Fig. 3. Conventional re-excitation measurement setting.

Set the solution sample on the top plate of the integrating hemisphere, and irradiate it with the excitation beam from above (Fig. 2).

If the system is configured as shown in Fig. 2, the excitation light transmitted through the phosphor solution sample is diffusively reflected inside the integrating hemisphere, and passes through the sample again to emit fluorescent light (re-excitation fluorescent emission). Since this emission is included in the measured light, some problems arise: for example, the fluorescent light level is estimated as more than its real value, or the quantity of the fluorescent light varies depending on the concentration of the sample.

It was first considered to eliminate the re-excitation fluorescent emission in the same way as with powder samples. We set the phosphor solution sample at some distance from the path of the excitation light as shown in Fig. 3 to estimate the quantity of the component of

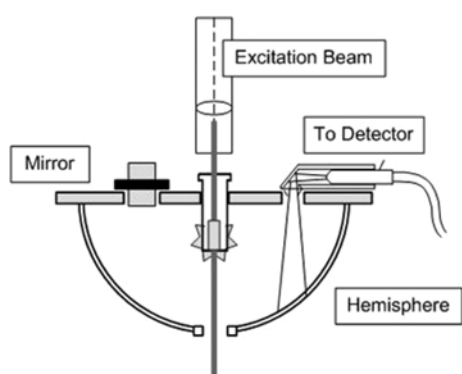


Fig. 4. New re-excitation measurement setting.

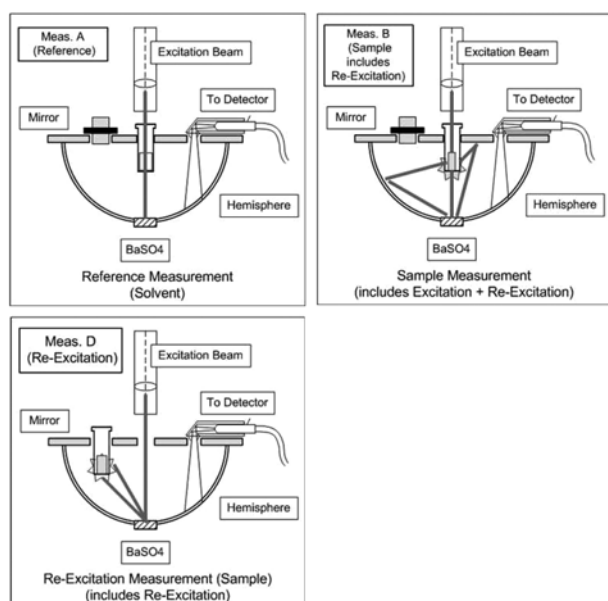


Fig. 5. Conventional measurement method of a solution sample (Meas. A: reference, Meas. B: sample, Meas. D: conventional Re-Excitation).

the re-excitation fluorescent emission, and subtract this quantity from that of the total fluorescent emission. In the system shown in Fig. 2, the excitation light coming through the sample increases as the sample's concentration decreases. As a result, the quantity of the re-excitation fluorescent emission component estimated in Fig. 3 increases but quantum efficiency decreases as the sample's concentration decreases.

Therefore, to eliminate the component of re-excitation fluorescent emission, the setup was devised as shown in Fig. 4 to capture only the fluorescent emission generated by the direct excitation by making a hole at the bottom of the integrating hemisphere to provide a path out of the integrating hemisphere for the excitation light passing through the sample.

Fig. 5, and steps (5-1) to (5-4) below, show the details of the conventional measurement method:

(5-1) Set the solvent only to measure the total excitation light, and calculate the number of excitation photons (Meas. A).

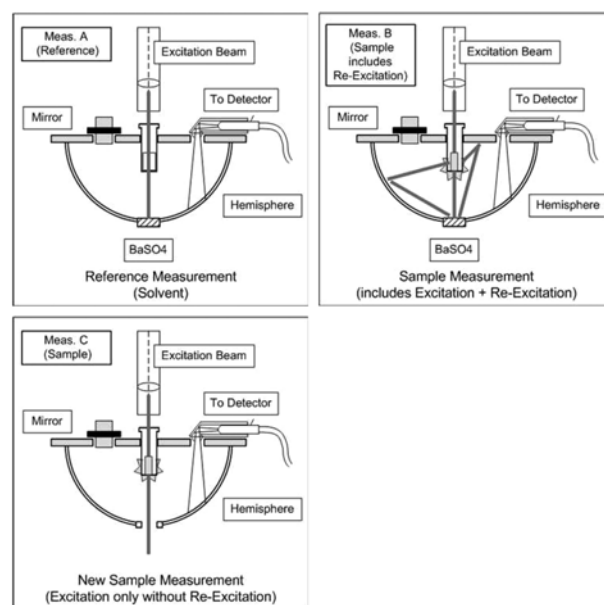


Fig. 6. New measurement method of a solution sample (Meas. A: reference, Meas. B: sample, Meas. C: new Re-Excitation).

(5-2) Set the sample to measure the excitation light transmitted through the sample and also the fluorescent light, and calculate the number of absorbed photons based on the calculation result of step (5-1). In addition, calculate the number of fluorescent photons including the component of the re-excitation fluorescent emission (Meas. B).

(5-3) Position the sample in the hole beside the central hole to measure the light. Estimate the quantity of the component of the re-excitation fluorescent emission to calculate the number of fluorescent photons generated by direct excitation (Meas. D).

(5-4) Calculate quantum efficiency by performing steps (5-1) to (5-3).

Next, Fig. 6 and steps (6-1) to (6-4) show the details of the new measurement method.

(6-1) Set the solvent only to measure the total excitation light, and calculate the number of excitation photons (Meas. A).

(6-2) Set the sample to measure the excitation light coming through the sample and also the fluorescent light, and calculate the number of absorbed photons based on the calculation result of step (6-1) (Meas. B). Do not use the fluorescent light value for calculation of quantum efficiency because this light includes the component of re-excitation fluorescent emission.

(6-3) Make a hole at the bottom of the integrating sphere with the sample set to measure fluorescent light, and calculate the number of fluorescent photons (Meas. C). Only the fluorescent light coming from direct excitation can be measured.

(6-4) Calculate quantum efficiency by performing steps (6-1) to (6-3).

Both the conventional and the new method were verified using standard fluorescent materials.

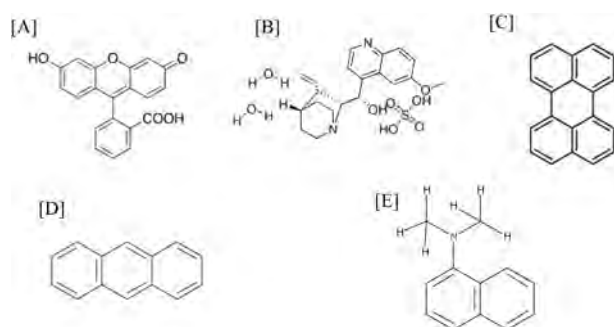


Fig. 7. Molecular Structure ([A] Fluorescein, [B] Quinine Sulfate, dihydrate, [C] Perylene, [D] Anthracene, [E] N,N-Dimethyl-1-aminonaphthalene).

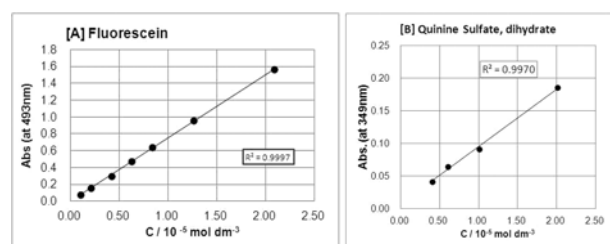


Fig. 8. Absorbance vs. Concentration Plot ([A] Fluorescein at 493 nm, [B] Quinine Sulfate, dihydrate at 349 nm).

Materials

The quantum efficiency values of known standard fluorescent materials were measured using the measurement system we've developed at this time. The values were compared with those available in the literature. The materials used were Fluorescein ($C_{20}H_{12}O_5$, MW: 332.306), Quinine Sulfate, dihydrate ($C_{40}H_{54}N_4SO_{10}$, MW: 782.96), Perylene ($C_{20}H_{12}$, MW: 252.31), Anthracene ($C_{14}H_{10}$, M.W: 178.23), and N,N-Dimethyl-1-aminonaphthalene ($C_{12}H_{13}N$, MW: 171.24) (Fig. 7). The excitation wavelengths were 493 nm (Fluorescein), 349 nm (Quinine Sulfate, dihydrate), 366 nm (Perylene), 365.5 nm (Anthracene), and 314 nm (N,N-Dimethyl-1-aminonaphthalene) respectively.

Results and Discussion

Linearity between the absorbance and concentration

Solutions of various concentrations were prepared for each sample, and quantum efficiency was measured in the region where a linear relationship consists (Lambert-Beer's law) between the absorbance and concentration of solution samples (2×10^{-5} to 4×10^{-6} mol dm^{-3}) (Fig. 8).

To compare the measured values with the literature values, the same solvent as in the literature for each material was used (Fluorescein: 0.1 M sodium hydroxide solution, Quinine Sulfate, dihydrate: 0.5 M sulfuric acid solution, Perylene, Anthracene: Ethanol, N,N-Dimethyl-1-aminonaphthalene: Cyclohexane).

In Fig. 8, relationship between the absorbance and the concentration for Fluorescein [A] and Quinine Sulfate, dihydrate [B] were shown as examples. For all

Table 1. Measurement results for Fluorescein by both the conventional and the new method.

C/ 10^{-5} mol dm^{-3}	Transmittance	Absorbance	Quantum Efficiency	
			Conventional	New
2.09	0.032	0.968	0.922	0.913
1.26	0.102	0.898	0.923	0.926
1.00	0.147	0.853	0.914	0.923
0.84	0.203	0.797	0.907	0.922
0.63	0.304	0.696	0.875	0.931
0.42	0.435	0.565	0.865	0.937
0.21	0.655	0.345	0.828	0.930
0.11	0.817	0.183	0.801	0.937
2.09	0.032	0.968	0.922	0.913
1.26	0.102	0.898	0.923	0.926
1.00	0.147	0.853	0.914	0.923
0.838	0.203	0.797	0.907	0.922
0.628	0.304	0.696	0.875	0.931

Table 2. Measurement results for Quinine Sulfate, dihydrate by both the conventional and the new method.

C/ 10^{-5} mol dm^{-3}	Transmittance	Absorbance	Quantum Efficiency	
			Conventional	New
2.01	0.564	0.436	0.644	0.577
1.01	0.734	0.266	0.594	0.566
0.604	0.827	0.173	0.55	0.573
0.403	0.882	0.118	0.445	0.575

Table 3. The measured quantum efficiency values for 5 materials by our system

Sample	Solvent	Quantum Efficiency	Literature Value
Fluorescein	0.1 M NaOH	0.901 ± 0.006	0.92 [2]
Perylene	EtOH	0.866 ± 0.019	0.87 [4]
Quinine sulfate dihydrate	0.5 M H_2SO_4	0.572 ± 0.008	0.55 [3]
Anthracene	EtOH	0.261 ± 0.002	0.27 ± 0.01 [2]
N,N-Dimethyl-1-aminonaphthalene	Cyclohexane	0.012 ± 0.001	0.011 [5]

materials we used these concentration regions, which consists linear relationship between the absorbance and the concentration for measurement of the quantum efficiency values.

Quantum efficiency values

Tables 1 and 2 show the measurement results of the quantum efficiency of Fluorescein and Quinine Sulfate, dihydrate on comparing the new method with the conventional one.

These two materials showed spectra with maximum fluorescent light at wavelengths of 513 - 515 nm and 457 nm, respectively.

The conventional method showed a trend that quantum efficiency decreased as the sample's concen-

tration decreased. By contrast, the new method showed that the quantum efficiency values were constant and independent of the sample's concentration; they were also found to be almost equal to the literature values, with 0.92 for the former [2] and 0.55 for the latter [3].

Values in Tables 1 and 2 indicate the quantum efficiency after re-excitation correction was compensated (by eliminating the component of the fluorescent light generated by the secondary excitation).

Table 3 shows the results of measured quantum efficiency values by our system and literature values for each. As shown in below, we investigated standard samples which have wide variation of literature value like between 1% and 92% (0.01 and 0.92). Each measured value agrees well with the literature value.

Conclusions

We have developed a quantum efficiency measurement system with an integrating hemisphere, which can measure solution samples easily. By using an integrating hemisphere, the ceiling works as a mirror and also works to hold the sample. Thus an integrating hemisphere system is easily used for both of powder samples [1] and solution samples.

To measure quantum efficiency value using this system, re-excitation fluorescent emission must be taken into account. When powder samples were measured, quantum efficiency was calculated by subtracting the quantity of the re-excitation fluorescent emission from that of the fluorescent emission including the fluorescent emission component generated by re-excitation. However, when solution samples were measured, it was found that quantum efficiency could be measured easily by making a hole at the bottom of the integrating hemisphere to eliminate the excitation light transmitted through the sample out of the integrating hemisphere.

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