Paper

Quantum Efficiency Measurement of Lamp Phosphors in Accordance with Radiometric Standards

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ABSTRACT

To measure the quantum efficiencies of lamp phosphors, a JCSS (Japan Calibration Service System) traceable measurement method that uses a polychromator, with improved optical design to reduce stray light, and an integrating sphere has been developed. To verify the measurement accuracy of this method, a monochromator, which has a 0°:45°x incident optical system, was used. The BRDF (Bidirectional reflectance Distribution Function) of the phosphor was measured by a goniophotometer. A comparison was made between these JCSS traceable measuring devices on the 260 nm to 400 nm wavelength characteristics of the internal quantum efficiency of the blue phosphor BAM (BaMgAl10O17 : Eu2+), which has excitation characteristics up to 400 nm. The results agreed within 4% of the difference of the measured values. This is a good agreement considering that it was a composite measure and that the uncertainty of the spectral irradiance standard in the spectral region is lower than 3%. It has also been established that the proposed method using a polychromator and an integrating sphere shows sufficient measurement accuracy.

KEYWORDS: fluorescent, quantum efficiency, lamp phosphor, polychromator, integrating sphere

1. Introduction

Lamp phosphors (hereinafter simply called phosphors) are the important components of fluorescent lamps and white LEDs, whose energy efficiency (light-emitting efficiency) is an important factor in determining the performance of the light source. Since the energy efficiency of phosphors is calculated based on their quantum efficiency, it is necessary to recognize the relation between energy efficiency and quantum efficiency as well as to measure quantum efficiency with high accuracy.

However, the measurement of phosphor quantum efficiency has been accomplished by composite measurement with the two stages of excitation and light-emission. In addition, excitation was measured in the ultraviolet range in which measurement is difficult, and the individuals performing spectro-radiometry were not very familiar with phosphors. So, measurement was mainly conducted by materials specialists. Thus, in the past, the quantum efficiency of phosphors was often measured in a manner that was not directly relevant to the traceability of spectro-radiometry. For example, comparative measurements were performed with standard phosphors whose history was not necessarily clear or the measuring devices were calibrated according to standards that were not associated with the current traceability system of spectro-radiometry (especially in the ultraviolet region).

In order to evaluate the energy efficiency of fluorescent lamps and white LEDs properly according to the spectro-radiometry system, the authors performed a series of trials to raise the accuracy of the composite measurement by measuring the quantum efficiency of phosphors using a spectral irradiance standard, which will lead to the traceability of spectro-radiometry, and measuring excitation and light emission using the same measurement system. This paper reports a summary of the methods and results.

2. Principles and problems of the quantum efficiency measurement method

2.1 Principles of quantum efficiency measurement

The external quantum efficiency of a phosphor is the ratio of the number of photons of the fluorescent emission to that of the excitation light irradiated to the phosphor. On the other hand, the internal quantum efficiency of a phosphor is the ratio of the number of photons of the fluorescent emission to that of the excitation light absorbed in the phosphor. The number of photons of the excitation light absorbed in the phosphor is calcu-
lated by subtracting the component that was not absorbed but was reflected by the phosphor from the number of photons of the excitation light irradiated to the phosphor.

This time, in the quantum efficiency measurements, the component of the reabsorbed fluorescent emission that was originally emitted by the phosphor itself inside its layer was not included in the number of fluorescent photons. In short, quantum efficiency to the number of the fluorescent photons emitted from the phosphor surface calculated by assuming that the phosphor measured is so thick that there is no transmitted light.

Figure 1 shows an example of the spectral distribution of the blue phosphor BAM (BaMgAl₁₀O₁₇ : Eu²⁺ : Nichia Corp.’s NP-107-5). As is shown in the figure, the excitation light spectrum irradiated to the phosphor, reflection spectrum and the fluorescent spectrum are given as \( E(\lambda) \), \( R(\lambda) \), and \( P(\lambda) \), respectively. The external and internal quantum efficiency, \( \eta_e \) and \( \eta_i \), are expressed by the following Formulas (1) and (2). Since the denominators and numerators of these formulas are the number of photons originally, the irradiation power must be divided by \( h \cdot c / \lambda \), which represents the energy of a photon with a wavelength of \( \lambda \). However, this \( h \cdot c \) (\( h \) : Planck’s constant and \( c \) : light speed) term can be cancelled out because it is in both the denominator and numerator.

\[
\eta_e = \frac{\int_{\lambda_1}^{\lambda_2} \lambda \cdot P(\lambda) \, d\lambda}{\int_{\lambda_1}^{\lambda_2} \lambda \cdot E(\lambda) \, d\lambda} \tag{1}
\]

\[
\eta_i = \frac{\int_{\lambda_1}^{\lambda_2} \lambda \cdot P(\lambda) \, d\lambda}{\int_{\lambda_1}^{\lambda_2} \lambda \cdot (E(\lambda) - R(\lambda)) \, d\lambda} \tag{2}
\]

The spectral measurement is conducted in the wavelength region from \( \lambda_1 \) to \( \lambda_2 \). As mentioned later, however, if \( E(\lambda) \), \( R(\lambda) \), and \( P(\lambda) \) are measured by a spectral measurement device (hereinafter simply called the spectroradiometer) equipped with the same optical system, the factors related to the measurement device will be cancelled out in both the numerator and denominator. So the quantum efficiency, \( \eta \), can be calculated by a simple comparative measurement method.

2.2 Problems of quantum efficiency measurement

As mentioned above, quantum efficiency measurement for phosphors is considerably more difficult than that in general spectro-radiometry. The reasons are as follows:

(1) Spectral irradiance measurement of the excitation light is carried out by spectral measurement in the ultraviolet region. So, if the target is a phosphor used for fluorescent lamps, high-precision measurement in a wavelength range of 250 nm to 260 nm is required.

(2) To measure the emission of phosphors, the spectral radiant emittance from the fluorescent surface must be measured. However, there is no standard light source for the spectral radiant emittance, so this value must be measured by irradiating the radiation from a standard light source for spectral irradiation onto a diffusive reflection surface whose spectral reflectance is already known and measuring the reflected component, which is regarded as the exitance of the spectral radiant flux. To do so, a reflective surface whose spectral reflectance is already known must be prepared separately.

(3) The uncertainty of quantum efficiency measurement is the sum (square sum) of these two types of measurement. Therefore, to keep the uncertainty of quantum efficiency measurement as equal as possible to the level of normal spectro-radiometry, higher accuracy is required for the measurements mentioned in steps (1) and (2).

The method of measuring the excitation light and fluorescence emission using the same optical system, which is mentioned in this paper, seems to be effective in raising the measurement accuracy.

3. A measuring device with an integrating sphere and its measurement method

Figure 2 shows an optical system to measure the quantum efficiency of phosphors by utilizing an integrating sphere. The measurement optical system is composed with two devices: One is a monochromatic excitation light source consisting of a Xe lamp with a grating spectroradiometer that generates a beam-like monochromatic excitation light with a wavelength between 250 nm and 400 nm. The other is an ultraviolet-
visible spectroradiometer having an integrating-sphere equipped with incident optical system that uses the same optical system to measure the beam-like excitation light, diffusive fluorescence emission from the phosphor surface, and reflected excitation light from the phosphor surface. The sample phosphor and BaSO₄ used as a standard for reflectance were pressed and attached to a cell with an inner diameter of 12 mm and a depth of 2 mm. The transmitted component is sufficiently small because of the thickness of this fluorescent layer.

The details of the optical system shown in Figure 2 are as follows:

(1) The size of the irradiated image of the excitation light on the phosphor surface was almost 5 mm × 5 mm, and the device was configured so that the center of the phosphor surface, which had an inner diameter of 12 mm, was illuminated. In addition, since it was expected that the specular reflection component would be included in the reflection spectrum RA of the excitation light on the phosphor surface, the incident angle of the excitation light onto the sample phosphor surface attached inside the integrating sphere was at around 5 degrees from the normal line of the phosphor surface.

(2) The excitation light source was configured with a Xe lamp (Hamamatsu Photonics’ L2195: 150 W, ozone-free type) and a grating monochromator (JOBIN-YVON’s H-10UV: the groove density of the grating was 1200/mm, the blaze wavelength was 250 nm, and f=100 mm). The half width of the wavelength of the obtained monochromatic light was almost 10 nm.

(3) An integrating sphere with an inner diameter of 60 mm captured the diffusive reflection light of the monochromatic excitation light from the BaSO₄ reflectance standard and the diffused reflection component and fluorescent emission component of the monochromatic excitation light from the surface of the sample phosphor, and a spectroradiometer, which was a poly-

chromator (Otsuka Electronics’ MCPD7000-28, special specification), measured their spectra.

(4) The BaSO₄ reflectance standard employed after its diffusive reflectance was calibrated by utilizing a Labsphere standard reflecting board (Spectralon SRS-99). For calibration, the optical system shown in Figure 2 was used.

The spectroradiometer used this time (Otsuka Electronics’ MCPD7000-28SR, special specification) was a device greatly reducing stray light in the ultraviolet range compared with conventional polychromators. Figure 3 shows a comparison between the output of the spectroradiometer (with dark signals eliminated) and that of a conventional polychromator when an ozone-free Xe lamp was measured. Measurement was conducted using a permeant diffusivity incident optical system with sandblast quartz at the tip. Although the spectrum of the ozone-free Xe lamp output nothing in the wavelength region of 230 nm or less, spectra remained seemingly due to stray light when the conventional polychromator was used. On the other hand, when the special specification MCPD7000-28SR spectroradiometer was used, stray light was reduced, and there was no spectral response in the wavelength region of 230 nm or less.

Stray light in a spectroradiometer coming from the measuring light enters the device through its incident slit.

This is primarily the scattering of the zeroth-order diffracted light that is not dispersed by the grating scatter inside the polychromator cell and noise consisting of light reflected on the detector surface and present inside the polychromator cell regardless of the wavelength. When the spectrum of a light source that has a large spectral intensity in the visible wavelength region is measured, such as a Xe lamp or lamp, the stray light becomes too large to ignore due to the small ultraviolet spectral intensity. When the quantum efficiency of a
phosphor is measured, the intensity of the ultraviolet spectrum of the excitation light is larger than that of the visible spectrum of the fluorescent emission. By this reason, stray light can be ignored. However, since a halogen lamp is used as a standard to calibrate the spectral responsibility of the spectroradiometer, if calibrated under strong stray light, the responsibility in the ultraviolet wavelength region with strong stray light shows a larger value than the actual one. So, some errors are caused; for example, the level of the excitation light is underestimated, but the quantum efficiency is measured as being higher than the actual value. Thus, we adopted a spectroradiometer notably reducing stray light for quantum efficiency measurement of phosphors this time.

3.1 Calibration of the spectroradiometer by utilizing an integrating sphere

As mentioned in Section 2.2, high measurement accuracy is required to perform spectral measurement on excitation light and fluorescent emission. The spectroradiometer including the optical system was calibrated in a traceable to the spectral irradiance standard provided by JCSS (Japan Calibration Service System), which is the certification agency for calibration based on the Measurement Act.

However, in this measurement, the incident light entering into the spectroradiometer is the reflected light (or fluorescent emission) from the reflective standard or the light gathered onto part of the sample fluorescent surface, as shown in Figure 2. Therefore, if the device is calibrated using the diffusive light from the spectral irradiance standard as shown in Figure 4, some uncertainty is caused. In the same case as applied to the ordinary spectroradiometer, reflecting light not from the standard reflecting surface or sample surface but from the inner wall of the integrating sphere (hereinafter simply called the inner wall) is also taken in. So, calibration was carried out in accordance with the following procedure:

(1) As an incident optical system to measure irradiance, a spectroradiometer equipped with a light-shielding tube having a diffusional permeability quartz plate (one of whose sides was finished with #200 sandblasted) at the tip was prepared. Then, as shown in Figure 5, it was calibrated using a lamp of the spectral irradiance standard, and its spectral responsibility $S(\lambda)$, was calculated.

(2) As shown in Figure 6, the beam of the zeroth-order light (white light) output by the monochromator of the monochromatic excitation light source was irradiated to the BaSO$_4$ reflectance standard. Since this BaSO$_4$ has almost perfect diffusive reflection, the spectroradiometer mentioned in step (1) was used to measure the spectrum reflected at an angle of 45°. The response at this stage $I_{\text{in}}(\lambda)$, is expressed by the formula below, given that the spectral distribution of the zero-dimensional diffraction light is $P_{\Delta}(\lambda)$ and the $0° : 45°$ x reflection coefficient of the standard reflecting board (BRDF) is $k_1R(\lambda)$. 

Figure 4  Schematic diagram of the optical system for calibrating the integrating sphere of a spectroradiometer against the spectral irradiance standard

Figure 5  Schematic diagram of the optical system for calibrating the diffuser head of a spectroradiometer against the spectral irradiance standard

Figure 6  Schematic diagram of the optical system for calibrating the 0-order diffraction ray of a monochromator against the spectral irradiance standard traceable to JCSS
by measuring re-excitation. If the sample phosphor has low reflectance and greatly absorbs the excitation energy, the fluorescent component excited by the excitation light that is first reflected on the sample surface, is then reflected on the inner wall of the integrating sphere repeatedly, and then enters the sample phosphor again (re-excited fluorescent emission) is small.

On the other hand, if the reflectance exceeds 50%, re-excitation becomes greater, so the corrected value of the internal quantum efficiency reaches around 10% of the measured value. As mentioned in the appendix, the integration efficiency $F$, which is left in the re-excitation term only, is proportional to $1/(4\pi r^2)$; thus, the radius $r$ of the integrating sphere is larger, the re-excited fluorescent emission becomes smaller. For the integrating sphere with the radius of 30 mm, which was not so long, is employed this time, so the re-excited fluorescent emission was large.

Thus, the fluorescent emission component generated by the re-excitation was eliminated in the manner described in the appendix.

4. A spectroradiometer and measuring method using a $0^\circ$ : $-45^\circ \times$ incident optical system

When measuring fluorescence using an integrating sphere, there is some error because of the use of the integrating sphere as described in Section 3. When considering such error, the problems of the reflectance and fluorescent emission of the fluorescent material can be avoided by measuring their spatial characteristics (light distribution) and then evaluating measured values using an optical system with an incident angle of $0^\circ$ : $45^\circ \times$. So, in order to verify the measured values of the above measurement method, which uses an integrating sphere, in a comparative manner, we conducted quantum efficiency measurement by adopting the $0^\circ$ : $45^\circ \times$ incident optical system shown in Figure 9.
The monochromatic excitation light source was configured with a Xe lamp (Hamamatsu Photonics’ L2195: 150 W, ozone-free) and a grating monochromator (Edmund) MINI-CHROM: the groove density of the grating is 2400/mm, the blaze wavelength is 250 nm, and f=74 mm. The beam-like excitation light from this light source was emitted into the sample phosphor perpendicularly. The variable region of the wavelength of the monochromatic radiation is 250 to 550 nm, and the half width of its wavelength band is 11 nm. For the fluorescent emission from the phosphor surface and the diffusive reflecting light of the excitation light from the phosphor surface, we measured the radiation in the 45° direction to the normal line of the sample phosphor surface by utilizing a grating spectroradiometer for spectral measurement (Edmunds MINI-CHROM: the groove density of the grating is 1800/mm, the blaze wavelength is 500 nm, and f=74 mm) and a photomultiplier tube (Hamamatsu Photonics’ R6356-6). When the spectrum was measured, the wave was modulated by a chopping frequency of 15 Hz and detected by a lock-in amplifier.

In order to use a reflectance standard, BaSO₄ was pressed and attached to a cell with an inner diameter of 18 mm and a depth of 5 mm, and its absolute reflectance was measured using the Taylor’s third method₃⁸.

The spectroradiometer for spectral measurement was calibrated as shown in Figure 10 by setting the reflectance standard in the position of the sample phosphor shown in Figure 9 and illuminating its surface with a halogen lamp (JC24V150W, distribution temperature 3235 K), which was a JCSS-traceable lamp of the spectral irradiance standard whose values were diverted from another one. The measurable wavelength region was 250 to 800 nm, and the half-width of the measurable wavelength band was 5 nm. The measuring wavelength interval was 2 nm for the spectral measurement of the excitation light and 5 nm for that of the fluorescence. A diaphragm was put on the light path to keep the apertures of the incident of the fluorescent excitation and that of the incident of the device calibration equal to each other.

### 4.1 Light distribution measurement of fluorescent emission

For both the reflectance standard and sample, the measured values were the values of 0°/45° BRDF (Bi-directional Reflectance Distribution Function) of the radiant flux, not the values of the total radiant flux. Therefore, if the light distribution is different depending on the sample, the ratio between the radiant intensity and whole-space radiant flux might not be the same, so quantum efficiency cannot be obtained correctly. By this reason, we measured the light distribution of the fluorescent emission of the sample at azimuths, ϕ, of 0° and 90° with an excitation wavelength of 365 nm, and an incident angle, θ, of 0° using an arm-like goniophotometer and the light distribution of the reflected light from the BaSO₄-attached surface with the light from the lamp emitted under the same incident condition. Figure 11 shows the light distribution characteristics of the blue phosphor BAM and the BaSO₄-attached surface used as the reflectance standard. In addition, Table 1 shows the ratio between the whole-space radiation flux, $\Phi$, and the 45° radiation intensity $I_{45}$. Although this ratio was almost consistent with between the BAM and BaSO₄, the reflective light distribution of a surface to which powders are attached differs depending on the grain diameter or powder type. Therefore, it seems to be necessary to confirm the characteristics of reflective light distribution when conducting quantum efficiency is measured using the 0°: 45° incident optical system.

### 5. Comparison of measured values between a measuring device equipped with an integrating sphere and a 0°:–45° incident optical system

We conducted comparative measurements for the blue phosphor BAM (BaMgAl₁₆O₁₉: Eu²⁺; Nichia Corp.’s NP-107-58) using optical systems with an integrating sphere and 0°: 45° incidence. Table 2 shows the differences of the two types of measuring optical systems.
Figure 11  Intensity distribution of BaSO₄ reflection and BAM phosphor fluorescence

Table 1  Ratio of total space radiant flux: $\Phi$ to radiation intensity in the 45° direction

<table>
<thead>
<tr>
<th></th>
<th>Blue phosphor BAM (NP-107-58)</th>
<th>BaSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi/\phi_{45}$</td>
<td>0.994 (4.308)</td>
<td>1.000 (4.338)</td>
</tr>
</tbody>
</table>

Table 2  Comparison of two quantum efficiency measurement systems

<table>
<thead>
<tr>
<th></th>
<th>System-A</th>
<th>System-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical system</td>
<td>Integrating Sphere</td>
<td>Traceable to JCSS</td>
</tr>
<tr>
<td>Spectral irradiance</td>
<td>Traceable to JCSS</td>
<td>Traceable to JCSS</td>
</tr>
<tr>
<td>Standard lamp</td>
<td>Spectralon-SRS-99 (Traceable to NIST standard)</td>
<td>Spectralon-SRS-99 (Traceable to NIST standard)</td>
</tr>
<tr>
<td>Reflectance standard</td>
<td>Polychrometer (MCPD-7700-28SR)</td>
<td>Monochrometer (MIMI-CHROM)</td>
</tr>
</tbody>
</table>

The two systems are mentioned as measuring devices A and B, respectively. Although the blue phosphors used for the measurements belonged to the same lot, they were not perfectly equal because their forming methods and shapes were different when their surfaces were pressed and attached. In addition, measuring devices A and B were being used by separate departments, respectively, and it was not possible to use the same spectral irradiance standard or reflectance standard, so the measurements were performed using the standards managed by the respective departments.

First, we compared the measured values of the spectral absorption rate in the excitation wavelength region (1-spectral reflectance). Table 3 shows the results. Although the traceability of the reflectance standard for each was independent, the measured values were consistent with each other within the difference of 3%. The results of A and B seem to be good agreement with each other for the following reasons: (1) The value of absolute reflectance for measuring device B was defined using an integrating sphere⁷, and the extended uncertainty of the spectral irradiance standard lamp used for the calibration was as large as 6% in the ultraviolet region (with a wavelength of 260–370 nm). (2) There was an uncertainty of 2% or more in the repeatability of the BaSO₄-attached surface, and (3) the value of the absolute reflectance was not defined every time measurement was conducted.

Next, we set an excitation wavelength region at 20-nm steps between 260 to 400 nm and compared the measured values of the external quantum efficiency for the respective excitation wavelengths. For measuring device A, the emission spectra of the respective wavelengths were measured five times with the same sample, and the measured values were averaged three times after scanning the excitation wavelengths. The dispersion of the respective measured values was within ±1% for the excitation wavelengths. As an example of the measurement, Figure 12 shows the fluorescent spectrum of the blue phosphor BAM (NP-107-58), which was measured on measuring device A with an excitation wavelength of 260 nm.

On the other hand, for measuring device B, the emission spectra of the same attached sample were measured. The spectra were measured five times for each
measuring wavelength at 2.5-nm intervals between 250 to 780 nm. The measured values were averaged by two times scanning the excitation wavelengths. Figure 13 shows the results of the external quantum efficiency measurement of the two measuring devices. The dispersion of the respective measured values was within ±2%. The two were consistent within a mutual difference of 3%. The external quantum efficiency is the ratio of the number of photons between the excitation light spectrum irradiated onto the phosphor and the fluorescent spectrum as shown by Formula (1), whose uncertainty is greatly influenced by that of the spectral irradiance standard. Although the standard of system-A was supplied by JEMIC (Japan Electric Meters Inspection Corporation), system B was supplied by ETL (Electrotechnical Laboratory at that time). At that time, JEMIC did not define the values of the spectral irradiance standard lamp by the spectral method but instead used a method of diverting the values of the spectral distribution by matching the distribution temperature of the lamp of a certain model so that the uncertainty was significant, especially in the ultraviolet region. Moreover, concerning to the spectral irradiance standard of the two, taking it into consideration of the routes for traceability being independent and that they were calibrated at different times, the measured values of the two seemed to be well consistent with each other because the difference in the measured values was within 3%.

In addition, it was found that the polychromator used for measuring device A reduced stray light sufficiently, because the measured values of this device A were consistent with the ones of measuring the device B utilizing a monochromator in the wavelength region of 300 nm or less. Since the polychromator’s stray light was greater than monochromator’s in the past, the calibration coefficient was set smaller by utilizing the energy of the stray light when the spectral responsivity of the measurement system was calibrated using the spectral irradiance standard lamp. As a result, the excitation energy in the ultraviolet wavelength region was evaluated as lower than it really was, and the quantum efficiency was evaluated as higher than it really was in the wavelength region of 300 nm or less. Since the measured values were consistent between the polychromator used this time and the monochromator due to the improvement of the optical system, stray light was reduced sufficiently.

The measuring device A had an optical system with an integrating sphere and corrected for re-excitation as described in Section 3.2. As shown in Figure 8, the blue phosphor BAM showed a surface reflectance of more than 30% in the excitation wavelength of 360 nm or more, so the re-excitation component became too large to ignore. However, the measured external quantum efficiency was consistent with that of measuring the device B equipped with a 0°: 45°x incident optical system generating no re-excitation within 3% of the difference in the measured values. So, the re-excitation correction method described in Section 3.2 seemed effective.

The difference in the measured values at an excitation wavelength of 400 nm is considered below. The flare of the excitation spectrum of the measuring device A at a wavelength of 400 nm or more overlapped with the fluorescent spectrum, so the fluorescent spectrum with a wavelength from 400 to 410 nm could not be separated from the excitation spectrum and was excluded from the calculation of the number of photons. On the other hand, for the measuring device B, when the fluorescent spectrum was measured at an excitation wavelength of 400 nm, the excitation spectrum was separated by utilizing a sharp cutting filter L41 (made of glass manufactured by Hoya Corp.). How to handle the wavelength region in which the excitation and fluo-
resonant spectra are superimposed on each other is a future theme for the polychromator.

Then, we compared the measured values of the internal quantum efficiency in the excitation wavelength range between 260 to 400 nm. Figure 14 and Table 4 show the results. The measured values of the two were consistent with each other within a difference of 4%. It seems that the difference in the measured values in the excitation wavelength range from 320 to 360 nm has been due to the difference in the spectral irradiance standards as described in the paragraph concerning the results of external quantum efficiency measurement.

6. Quantum efficiency of the blue phosphor BAM at an excitation wavelength of 260 nm

We have been considering the measurement method since the report issued in 199723 to establish the technology for the directly measurement of the quantum efficiency of phosphors by utilizing radiation. Concerning the reports issued in 199723 and 199945, to eliminate the influence of stray light on the polychromator used at those times, a thermal radiation detector with a sensitivity that was constant to the wavelength was applied to calibrate the integrating sphere optical system. In 2008, we adopted a polychromator that was improved by utilizing a technology to reduce stray light and an integrating sphere and measured quantum efficiency by a JCSS-traceable spectral measurement method9. Moreover, in 2009, to verify the measured values of the above measurements, quantum efficiency was measured by a 0°:45°x optical system with a monochromator using a spectral irradiance standard whose JCSS-traceability route was independent. In the studies in 2008 and 2009, measured values were evaluated using phosphors belonging to the same lot. Table 5 shows the history of the measured values. As a result of adopting such different types of calibration methods and traceability, the measured internal quantum efficiency of the blue phosphor BAM was 0.846 on average (standard variation σ=0.008). Therefore, the internal quantum efficiency seems to be 0.84 to 0.86.

7. Conclusion

In order to measure the quantum efficiency of phosphors, we considered establishing a JCSS-traceable measurement method by adopting an integrating sphere and polychromator whose stray light was reduced owing to the improvement of the optical design. Moreover, to verify the accuracy of the measured values collected by this measuring method, we applied a JCSS-traceable measuring device utilizing a monochromator equipped with a 0°:45°x incident optical system and compared the measured values of the wavelength characteristics of the internal quantum efficiency in the wavelength range from 260 to 400 nm using a blue phosphor of BAM (BaMgAl10O17 : Eu2⁺), that has an excitation characteristic up to a wavelength of 400 nm for

![Figure 14 Internal quantum efficiency of blue phosphor BAM (NP-107-58) measured by system A & B](image)

Table 4: Internal quantum efficiency of blue phosphor BAM measured by system A & B

| W. L. (nm) | System-A | System-B | Difference | |Difference|/ Average (%) |
|-----------|----------|----------|------------|------------------|---------------|
| 260       | 0.841    | 0.847    | -0.006     | 0.7              |
| 280       | 0.885    | 0.869    | 0.016      | 1.8              |
| 300       | 0.914    | 0.917    | -0.003     | 0.3              |
| 320       | 0.929    | 0.899    | 0.030      | 3.3              |
| 340       | 0.941    | 0.904    | 0.037      | 4.0              |
| 360       | 0.942    | 0.914    | 0.028      | 3.0              |
| 380       | 0.874    | 0.865    | 0.009      | 1.1              |
| 400       | 0.811    | 0.844    | -0.033     | 4.0              |

Table 5: Measurement records for blue phosphor BAM (BaMgAl10O17 : Eu²⁺) excited by 260 nm radiation

<table>
<thead>
<tr>
<th>Report date</th>
<th>Report</th>
<th>Internal Q. E.</th>
<th>Traceability for power</th>
</tr>
</thead>
<tbody>
<tr>
<td>1997</td>
<td>267 Phosphor Research Society Meeting</td>
<td>0.840</td>
<td>Thermal radiation detector</td>
</tr>
<tr>
<td></td>
<td>(Measured by Panasonic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Measured by Panasonic)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2008</td>
<td>Annual Conf. of IEI, Jpn.</td>
<td>0.841</td>
<td>Spectral irradiance Standard lamp</td>
</tr>
<tr>
<td></td>
<td>(Measured by Otsuka)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2009</td>
<td>Annual Conf. of IEI, Jpn.</td>
<td>0.847</td>
<td>Spectral irradiance Standard lamp</td>
</tr>
<tr>
<td></td>
<td>(Measured by Saitama Univ.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.846</td>
<td>0.846</td>
<td>(σ=0.008)</td>
</tr>
</tbody>
</table>
the fluorescent lamp. This resulted in the measured values of the two measuring devices being consistent with each other within a difference of 4%. This seemed relatively good consistency taking into consideration that the measurements were composite and that the extended uncertainty of the spectral irradiance standard itself was 6% in this wavelength region. In addition, it became clear that sufficient measurement accuracy can be obtained by employing the JCSS-traceable measurement method utilizing a polychromator and integrating sphere, which we proposed this time.

Measurement using the optical system with an integrating sphere has the advantage that the influence of outside light can be excluded because of a closed space of the integrating sphere being used. On the other hand, excitation light reflected on the phosphor surface is reflected repeatedly on the inner wall of the integrating sphere and re-excites the phosphor. The error of this re-excitation was a problem. However, this problem was overcome by correction using the method shown in the appendix. Meanwhile, although the 0°−45° incident optical system does not have the problem of re-excitation, it is necessary to correct the measured values by measuring the reflection from the reflectance standard and sample phosphor as well as the light distribution of the fluorescent emission. Therefore, the integrating sphere is useful for the routine evaluation of phosphors.

The polychromator can reduce the stray light to a level that is almost equal to that of the monochromator, and the measurement time is shorter than that of the monochromator. So, the polychromator will likely be a popular choice as a special device to evaluate phosphors.

References


Annex

Estimation of the fluorescent emission due to re-excitation inside an integrating sphere

When the fluorescent spectrum of the sample phosphor is measured, the excitation light reflected on the phosphor surface is diffusively reflected inside the integrating sphere, and enters the phosphor again, and then emits fluorescence (fluorescent emission by re-excitation). We considered the influence of this re-excited fluorescent emission on the measured values.

As shown in Figure 7, a perfect diffusion sample with reflectance \( \rho \) attached to the inside of an integrating sphere with a radius of \( r \) is illuminated through the window on the sphere by light with a radiant flux of \( \phi_a \) (W). Given that the reflective intensity of the sample in the perpendicular direction is \( I_\theta \) (W/sr), there is a relation like that shown below:

\[
I_0 = \phi_a \cdot \frac{\rho}{\pi}
\]

Here, as shown in Figure A-1, the radiant illuminance \( E_{\alpha,0} \) at the point A on the inner wall in the angle \( \alpha \) direction from the sample’s normal line is expressed with the radiant intensity \( I(\alpha) = \phi_a \cos \alpha \) of the light source in the angle \( \alpha \) direction as shown in the formula below.

\[
E_{\alpha,0} = \frac{I(\alpha) \cdot \cos \theta / (2r \cdot \cos \alpha)^2}{\phi_a / 4 r^2} = \frac{\phi_a \cdot \rho}{(4 \pi r^2)}
\]

As clearly shown by Formula (A-2), \( E_{\alpha,0} \) does not depend on angle \( \alpha \) but is kept constant, so the inner wall is illuminated at an even illuminance. If the reflectance \( P_w \) (the inner wall uniformly performs diffusive reflection) and \( ds \) (the area of microsurface \( A \) on the wall) are given, the light flux reflected from microsurface \( A \). \( \phi_a \) is expressed by the following formula:

\[
\phi_a = \rho_w \cdot \frac{E_{\alpha,0} \cdot ds}{(\phi_a \cdot \rho_w / 4 \pi r^2) \cdot ds}
\]

If we define micro-surface B as a micro-surface on the wall in the angle \( \theta \) direction to the normal line of microsurface A, the radiant intensity in the direction from A to B, \( I_{\theta}(\theta) \) is expressed by the following formula if A is an uniformly-diffusive reflection surface:
\[ I_a(\theta) = \varphi_a \cdot \cos \theta / \pi \]  

(A-4)

Since B is a surface on the inner wall, the incident angle of \( I_a(\theta) \) to B is \( \theta \), and the distance between A and B is \( 2r \cdot \cos \theta \), the radiant illuminance of the radiant intensity \( I_a(\theta) \) on B, \( E_{ab} \) is expressed by the following formula:

\[
E_{ab} = I_a(\theta) \cdot \cos \theta / (2r \cdot \cos \theta)^2 = \varphi_a \cdot \rho_w \cdot \rho_e \cdot \rho_l / (4n^2r^2) \cdot ds / (4n^2r^2) \quad \text{(A-5)}
\]

As clearly shown in Formula (A-5), the reflected light from A does not depend on the outgoing angle from A, \( \theta \), so any part of the inner wall is illuminated by a uniform illuminance. On the other hand, the radiant illuminance on B, \( E_{b1} \), which is provided by the primary reflective light from the whole inner wall on which illuminance is uniform due to the reflected light from the sample, can be expressed by the following formula by integrating \( I(a) \cdot ds \) over the whole space:

\[
E_{b1} = \varphi_e \cdot \rho_w \cdot \rho_l / (4n^2r^2) \quad \text{(A-6)}
\]

Likewise, the radiant illuminance of the secondary reflected light \( E_{b2} \), which is originally the primary reflected light from the inner wall that is reflected on the wall again, is expressed by Formula (A-7), as shown below:

\[
E_{b2} = \varphi_e \cdot \rho_w^2 \cdot \rho_e \cdot \rho_l / (4n^2r^2) \quad \text{(A-7)}
\]

As mentioned above, the inner wall is illuminated uniformly, and \( E_{b1} = E_{a1} \) and \( E_{b2} = E_{a2} \) are true. Therefore, the radiant illuminance of point A, \( E_{at} \), is expressed by the following formula:

\[
E_{at} = E_{a0} + E_{a1} + E_{a2} \cdots = (\varphi_e \cdot \rho_l / (4n^2r^2)) \cdot (1 + \rho_w + \rho_w^2 + \rho_w^3 \cdots) = (\varphi_e \cdot \rho_l / (4n^2r^2)) \cdot 1 / (1 - \rho_w)
\]  

(A-8)

In the formula above, \( F \) is the integration efficiency of the integrating sphere expressed by the formula below:

\[
F = 1 / (4n^2r^2) \cdot 1 / (1 - \rho_w)
\]  

(A-9)

In other words, if radiation is reflected on the sample surface and repeatedly on the inner wall, and illuminates the sample again, the radiant illuminance is equal to \( E_{at} \). So if it is given that the surface area \( S \) of the sample and the excitation light from outside the integrating sphere illuminates the sample surface in proper quantities, the radiation \( P_e \) excited to the sample, is expressed by the following formula:

\[
P_e = \varphi_e + E_{at} \cdot S
\]  

(A-10)

Assuming that the sample is a phosphor and that the excitation light is converted into fluorescent emission with a energy conversion efficiency of \( \vartheta \). If the reflectance of the inner wall is \( \rho_w \) for both the excitation and fluorescent wavelengths, the illuminance of the wall by the fluorescent emission \( E_{wp} \) is like that shown below:

\[
E_{wp} = \theta \cdot (\varphi_w + E_{at} \cdot S) \cdot (1 - \rho_w) \cdot F = \theta \cdot \varphi_w \cdot (1 - \rho_w) \cdot F + \vartheta \cdot \varphi_e \cdot (1 - \rho_w) \cdot \rho_e \cdot F^2 \cdot S
\]  

(A-11)

The \( F^e \) term in Formula (A-11) is the re-excited fluorescent emission component excited again by reflection.
on the inner wall.

In order to eliminate this component, the exciting radiation of radiant flux $\varphi_e$ is not provided to the sample phosphor directly, but is provided to the inner wall as shown in Figure A-2. Here, the illuminance of the inner wall, $E_{aw}$, is expressed in the same manner as Formula (A-8) and like that shown below:

$$E_{aw} = \varphi_e \cdot \rho_w \cdot F$$  \hspace{1cm} (A-12)

Since the sample phosphor is excited by this wall-face illuminance only, the excitation light is converted into fluorescent emission at an efficiency of $\vartheta$ in the same manner as Formula (A-11). And the illuminance of the inner wall provided by the fluorescent emission, $E_{arp}$, is expressed by the following formula:

$$E_{arp} = \vartheta \cdot \varphi_e \cdot (1-\rho_s) \cdot F^e \cdot \rho_w \cdot S$$  \hspace{1cm} (A-13)

The illuminance provided by the re-excited fluorescent emission, $E_{arp}$, is multiplied by the ratio between the reflectance of the sample, $\rho_s$, and that of the inner wall $\rho_w$, at the excitation wavelength. Then, the product is subtracted from the illuminance of the inner wall provided by the fluorescent emission $E_{ap}$. This is expressed by the following formula:

$$\vartheta \cdot \varphi_e \cdot (1-\rho_s) \cdot F = E_{ap} - (\rho_s/\rho_w) \cdot E_{arp}$$  \hspace{1cm} (A-14)

When the exciting radiant flux $\varphi_e$ is irradiated to a standard reflecting board whose reflectance $\rho_s$ is known, the illuminance of the inner wall $E_{aw}$ is expressed by Formula (A-8). So, Formula (A-14) is expressed like that below:

$$\vartheta \cdot [(1 - \rho_s)/\rho_s] \cdot E_{aw} = E_{ap} - (\rho_s/\rho_w) \cdot E_{arp}$$  \hspace{1cm} (A-15)

Consequently, energy conversion efficiency $\vartheta$ is expressed by the following formula:

$$\vartheta = (E_{ap} - (\rho_s/\rho_w) \cdot E_{arp})/[(1 - \rho_s)/\rho_s] \cdot E_{aw}$$  \hspace{1cm} (A-16)

Although such a consideration concerns energy conversion efficiency, it is also applicable to quantum efficiency. $E_{arp}$ that is a term to exclude the re-excited component is a term consisting of $F^e$, as clearly shown by Formula (A-13). And $E_{aw}$ is a term consisting of $F$ only. Therefore, it is the primary term of $F$ that remains in the re-excited component under an energy conversion efficiency of $\vartheta$. The integrating efficiency of $F$ is proportional to $1/(4\pi r^2)$, so in case of using the larger the integrating sphere, the influence caused by the re-excitation will be smaller.

The optics model that I showed here is effective only when a sample area is small enough for size of the integrating sphere.