

BS EN 62607-3-1:2014



BSI Standards Publication

# Nanomanufacturing — Key control characteristics

Part 3-1: Luminescent nanomaterials —  
Quantum efficiency

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This British Standard is the UK implementation of EN 62607-3-1:2014. It is identical to IEC 62607-3-1:2014. It supersedes BS IEC 62607-3-1:2014 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee NTI/1, Nanotechnologies.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Luminescent nanomaterials - Quantum efficiency  
(IEC 62607-3-1:2014)**

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(IEC 62607-3-1:2014)

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## Foreword

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**Annex ZA**  
(normative)

**Normative references to international publications  
with their corresponding European publications**

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

NOTE 1 When an International Publication has been modified by common modifications, indicated by (mod), the relevant EN/HD applies.

NOTE 2 Up-to-date information on the latest versions of the European Standards listed in this annex is available here: [www.cenelec.eu](http://www.cenelec.eu).

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# INTERNATIONAL ELECTROTECHNICAL COMMISSION

## NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS

### Part 3-1: Luminescent nanomaterials – Quantum efficiency

#### FOREWORD

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International Standard IEC 62607-3-1 has been prepared by IEC technical committee 113: Nanotechnology standardization for electrical and electronic products and systems.

The text of this standard is based on the following documents:

FDIS	Report on voting
113/214/FDIS	113/219/RVD

Full information on the voting for the approval of this standard can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.



A list of all parts of the IEC 625607 series, published under the general title *Nanomanufacturing – Key control characteristics*, can be found on the IEC website.

The committee has decided that the contents of this publication will remain unchanged until the stability date indicated on the IEC web site under "<http://webstore.iec.ch>" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

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## INTRODUCTION

One of the principal drivers of solid-state lighting (SSL) is the potential efficiency of the illumination devices to convert electricity into light. Incandescent and fluorescent lighting devices are only about 5 % to 30 % efficient, with incandescent lighting having the lowest efficiency. Since a significant portion of all electricity consumed is used in providing lighting, increasing the efficiency of lighting devices will have a huge impact on the world's energy consumption. The luminous efficiency of SSL devices is a critical measurement of their overall efficiency, and standard methods to perform these measurements have been established and were essential to producing reliable product information for manufacturers and consumers. The same is true of the luminescent materials on which these light-emitting diode (LED) manufacturers rely; however, no such standard currently exists. This standard provides SSL manufacturers a universal means for comparing luminescent nanomaterials from different suppliers, and potentially for luminescent materials for LEDs in general.

The most common SSL devices are composed of a blue light-emitting diode (LED) and a luminescent material. The blue LED optically excites the luminophore, which will radiate light of the appropriate colour or colours to yield the desired white spectrum. This device, termed a phosphor-converted light emitting diode (or pc-LED), converts the electricity indirectly into white light by first creating blue light and then converting the blue light into broad-band visible radiation. Currently, quantum dots (QDs) or nanophosphors are one option for the photoluminescent material that converts the blue LED wavelength to broad spectrum visible light. QDs and nanophosphors are of interest in this application for several reasons including their greater colour flexibility, narrowband emission spectrum, broadband absorption, near-infinite flocculation time, reduced bleaching, and lower scattering compared to conventional phosphors which are typically larger than 5  $\mu\text{m}$ . QD-enabled pc-LEDs have been shown to have the best possible combination of colour rendering, correlated colour temperature, and luminous efficiency of any other pc-LED on the market.

A critical measurement parameter for luminescent materials used in the lighting industry is quantum efficiency, which is defined in this standard as the number of photons emitted into free space by a luminescent nanoparticle divided by the number of photons absorbed by the nanoparticle. Suppliers of QDs and luminescent nanomaterials typically measure only relative quantum efficiency (or alternatively, quantum yield) in the solution phase due to the ease of such measurements and the applicability of such measurements to biomedical imaging (a widespread use of QDs in R&D). These measurements are often taken at low concentrations where effects such as nanoparticle agglomeration and re-absorption are minimized. However, in end-use applications, the actual concentration of luminescent nanomaterials may be significantly different. For example, concentrated luminescent nanoparticle formulations (in either solid or liquid state) may be required to achieve a desired luminous flux and correlated colour temperature in a SSL device. This standard codifies that method for the first time, and establishes an absolute quantum efficiency test method for both solid (e.g., luminescent nanoparticles embedded in polymer matrices, coated on glass optics, applied directly to light emitted diodes, and other form factors) and solution samples (e.g., colloidal suspensions of luminescent nanoparticles), enabling suppliers and purchasers to compare the performance of one material to another, both in their raw (solution) phase as well as their technologically relevant (solid) phase of matter.

# NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS

## Part 3-1: Luminescent nanomaterials – Quantum efficiency

### 1 Scope

This part of IEC 62607 describes the procedures to be followed and precautions to be observed when performing reproducible measurements of the quantum efficiency of luminescent nanomaterials. Luminescent nanomaterials covered by this method include nano-objects such as quantum dots, nanophosphors, nanoparticles, nanofibers, nanocrystals, nanoplates, and structures containing these materials. The nanomaterials may be dispersed in either a liquid state (e.g., colloidal dispersion of quantum dots) or solid-state (e.g., nanofibers containing luminescent nanoparticles). This standard covers both relative measurements of liquid state luminescent nanomaterials and absolute measurements of both solid and liquid state nanomaterials.

### 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

CIE 017/E:2011, *International Lighting Vocabulary*

### 3 Terms and definitions

For the purposes of this document, the terms and definitions given in CIE 017/E:2011 as well as the following terms and definitions apply.

NOTE See also ISO TS 80004-2 (in preparation).

#### 3.1

##### **absorbance**

negative base 10 logarithm of the ratio of the intensity of light ( $I$ ) that has passed through and transmitted by a sample to the incident intensity ( $I_0$ ) at a specified wavelength

Note 1 to entry: Expressed mathematically, absorbance =  $-\log(I/I_0)$ . Proper corrections are required for other losses (e.g., reflection and scattering) for this equation to be correct.

#### 3.2

##### **absorptance**

ratio of the radiant or luminous flux in a given spectral interval that is absorbed by a medium to that of the incident light source

Note 1 to entry: The sum of the hemispherical reflectance, the hemispherical transmittance, and the absorptance is one.

#### 3.3

##### **absorption**

process by which matter removes photons from incident light and converts it to another form of energy such as heat

Note 1 to entry: All of the incident photon flux is accounted for by the processes of absorption, reflection, and transmission.

### **3.4**

#### **collimated incident light method**

method of determining absolute quantum efficiency that utilizes a collimated light beam, such as a laser, which is introduced into an integrating sphere containing the sample to be measured

### **3.5**

#### **diffuse incident light method**

a method of determining absolute quantum efficiency that utilizes a diffuse light beam from a laser, light emitting diode or other source, which is introduced into an integrating sphere containing the sample to be measured

### **3.6**

#### **matrix**

components of a sample other than the material being analyzed

Note 1 to entry: Matrix materials are typically inert organic or inorganic materials that contain luminescent nanoparticles.

### **3.7**

#### **nanomaterial**

classification of materials that encompasses both nano-objects and nanostructured materials

Note 1 to entry: Nano-objects are materials with one, two, or three dimensions in the size range from 1 to 100 nanometres.

### **3.8**

#### **optical density**

#### **OD**

negative base 10 logarithm of the ratio of the intensity of light that has passed through a sample, at a specified wavelength, to the intensity of the incident light source at that wavelength

Note 1 to entry: The abbreviation for optical density is OD. The optical density and absorbance of a sample are the same, if reflection losses have first been taken into account.

### **3.9**

#### **photobleaching**

phenomenon occurring in luminescent nanomaterials in which the fluorescent characteristic of the nanomaterial is degraded or destroyed by the light exposure necessary to initiate photoluminescence

Note 1 to entry: The net result of photobleaching is a decrease in quantum efficiency over time.

### **3.10**

#### **photobrightening**

phenomenon occurring in quantum dots and other luminescent nanomaterials in which the intensity of light emission from the nanomaterials, at a constant incidence flux, gradually increases over a period of time

Note 1 to entry: The net result of photobrightening is an increase in quantum efficiency over time.

### **3.11**

#### **power conversion efficiency**

ratio of the optical power in the emitted radiation divided by the optical power required to produce the radiation

### 3.12

#### **quantum dot**

semiconductor nanocrystal that exhibits size dependent properties due to quantum confinement effects on the electronic states

### 3.13

#### **quantum efficiency**

efficiency of photon emission from luminescent nanoparticles

Note 1 to entry: Quantum efficiency is also known as quantum yield.

Note 2 to entry: Quantum efficiency for luminescent nanomaterials is the ratio of the number of emitted photons to the number of absorbed photons. For the purposes of this standard, the measured quantum efficiency is a measure of the photons radiated by the luminescent nanomaterials into free space, and is more a measure of external quantum efficiency.

### 3.14

#### **relative quantum efficiency**

quantum efficiency measured relative to that of a well-characterized standard reference material

### 3.15

#### **absolute quantum efficiency**

quantum efficiency determined by measuring a value directly proportional to the number of photons emitted and absorbed

Note 1 to entry: The calibration standards used to determine absolute quantum efficiency shall be traceable to primary standards or national reference standards (e.g. NIST).

### 3.16

#### **external quantum efficiency**

ratio of the total number of photons emitted into free space by a luminescent material to the number of photons absorbed by the material

Note 1 to entry: For the purposes of this standard, external quantum efficiency (EQE) and quantum efficiency are used interchangeability.

### 3.17

#### **internal quantum efficiency**

ratio of the total number of photons emitted by a luminescent material internal to a device or material, to the number of photons absorbed by the material, regardless of whether the photons are emitted into free space

Note 1 to entry: The distinction between internal quantum efficiency (IQE) and external quantum efficiency (EQE) is that IQE includes all photons emitted by a luminescent material whereas EQE includes only those photons emitted into free space.

### 3.18

#### **radiant energy**

#### **Q**

energy travelling as electromagnetic waves

Note 1 to entry: Radiant energy is usually expressed in joules or watts times seconds. A quantum of radiant energy is a photon.

### 3.19

#### **radiant flux**

#### **Φ**

time rate flow of radiant energy

Note 1 to entry: Radiant flux is typically expressed in watts

### 3.20

#### **spectral radiant flux**

radiant flux per unit wavelength interval at a given wavelength ( $\lambda$ )

Note 1 to entry: Spectral radiant flux is typically denoted by  $\Phi_\lambda$ , which is equivalent to  $d\Phi/d\lambda$ , and is usually expressed in units of watts per nm.

### 3.21

#### **standard reference material**

##### **SRM**

material which has been characterized to be sufficiently homogeneous and stable with respect to one or more specified properties

Note 1 to entry: SRMs are accompanied by a certificate which certifies the values of these properties that have been established with traceability to the accurate realization of the unit and each certified value includes a stated uncertainty with a given level of confidence (see also SIPM Metrology brochure, 2<sup>nd</sup> edition, December 2003).

## 4 General notes on tests

### 4.1 General

It is recommended that good laboratory practices be exercised in conducting measurements on the quantum efficiency of luminescent nanomaterials as described in this document. In particular, the area where measurements are taken should be clean and free of dirt and debris and their sources.

### 4.2 Ambient conditions

Test equipment shall be located in an area with stable ambient ( $25 \pm 2$ ) °C, relative humidity, and consistent air flow. Locations underneath heating, ventilation, or air conditioning vents or by large fans shall be avoided since the change in air movement may adversely impact measurements. Ambient room temperature shall be measured in a consistent manner and reported with test results. When measuring room temperature, the temperature sensor shall be shielded from direct optical radiation from any source.

In addition, since stray light could influence the measurement results, background lighting should be held to the lowest possible level during all measurements.

### 4.3 Photobrightening and photobleaching

When irradiated with high intensity excitation sources, luminescent nanoparticles can exhibit both photobrightening (where the emission efficiency of the material increases during irradiation) and photobleaching (where the emission efficiency decreases during irradiation). Photobrightening can be either reversible (whereby the efficiency equilibrates to the original value once the excitation source is removed from the sample) or irreversible. Photobleaching is often irreversible due to physical damage or degradation of the material. These two phenomena can lead to erroneous efficiency measurements and therefore, care should be taken to eliminate or reduce their effects during measurement by closely monitoring the light exposure history of the sample. Consideration should be given to the excitation power applied to the sample (should be minimized while not sacrificing signal-to-noise) as well as the exposure time the excitation is applied to the sample (should be kept to a minimum while not sacrificing signal-to-noise).

### 4.4 Luminescence from contaminants at illumination wavelengths < 380 nm

Airborne contaminants such as smoke, hydrocarbons and fabric lint can accumulate in an integrating sphere over time. These contaminants can fluoresce under UV irradiation (< 380 nm) and hence cause attenuation of excitation signal and/or emission signal. In addition, some highly reflecting materials used for coating the integrating spheres may exhibit intrinsic parasitic emissions that cannot be removed by cleaning the sphere. The fluorescence

effect is amplified because of multiple reflections inside the integrating sphere. Therefore, it is important to characterize the fluorescence properties of the integrating sphere and make suitable corrections particularly while conducting measurements with UV excitation sources. Procedures are available for correcting for this stray luminescence [1,2]<sup>1</sup>.

#### 4.5 Industrial hygiene

Limited information is presently available on the environmental, health, and safety effects of nanomaterials in general. As such, the effects of human exposure to nanomaterials are unknown, however international exposure standards are under development. Prudent laboratory methods should be followed to minimize exposure to nanomaterials until additional information is available. Information and recommendations on the safe handling of nanomaterials are available and should be consulted.

NOTE One reference is U.S. National Institute for Occupational Safety and Health publication 2009-125 [3].

### 5 Measurement of relative quantum efficiency of nanomaterials

#### 5.1 General

Relative measurements of quantum efficiency are performed using a standard reference material with well-characterized properties. Due to the widespread use of relative measurement methods, there are a number of references that describe the instrumentation and setup procedures for fluorescence measurements [4, 5, 6, 7]. An example of a standard reference material used in relative quantum efficiency measurements is the use of a fluorescent organic dye of known quantum efficiency in determining the quantum efficiency of a colloidal suspension of quantum dots. Examples of the quantum efficiency of some typical standards can be found elsewhere [8]. The initial step of this procedure is to prepare a calibration curve over a specific spectral region using the fluorescent organic dye. The quantum efficiency of a sample is then determined relative to this calibration curve. Measurements of this type are typically performed on liquid-phase materials, as the fluorescent dye standards may be readily produced as liquid solutions of known concentrations.

#### 5.2 Test equipment

##### 5.2.1 Required supplies and test equipment

Test equipment for relative measurements of quantum efficiency shall include the following:

- standard fluorescence quartz cuvette of known path length. In the discussion below, it is assumed that cuvettes with a path length of 10 mm are used. If different sizes of cuvettes are used, appropriate adjustments in solution volumes may be necessary;

NOTE Incomplete cleaning of the cuvettes may leave residues that could negatively impact quantum efficiency measurements. It is good practice to acid-wash all quartz cuvettes before use to ensure that all residual quantum dots are removed from the cuvette prior to measurements.

- microbalance;
- microsyringe;
- spectrophotometer with diffuse transmittance capability that measures absorption over the spectral region of interest (typically the ultraviolet and visible (UV-Vis) regions). Wavelength calibration of the spectrophotometer should be verified at least annually using a light source of well-characterized emission wavelengths, such as a mercury argon calibration source;
- fluorescence spectrophotometer capable of producing excitation radiation in the spectral region of interest (typically UV-Vis) and measuring the excitation and emitted radiation. Additional information on the setup and calibration of fluorescence spectrophotometers

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<sup>1</sup> Numbers in square brackets refer to the Bibliography.

can be found elsewhere [4, 5, 6, 7,9,13]. Typically the excitation radiation is produced by a monochromated discharge lamp with an adjustable slit at the exit of the monochromator to control peak full-width-at-half-maximum (FWHM). Emitted radiation from the sample typically passes through additional optics including an emission slit and monochromator, and then strikes the detector (e.g., photomultiplier tube). A calibration file for the spectral response of the emission monochromator and detector is needed and should either be obtained from the instrument manufacturer or created from a calibrated light source.

## 5.2.2 Test equipment setup

### 5.2.2.1 UV-Vis spectrophotometer

The UV-Vis spectrophotometer shall be set to scan the spectral region of interest, which is typically set from 300 nm to 800 nm. Acquisition parameters for the spectrophotometer shall be adjusted to achieve an optimal signal-to-noise ratio. For example, the minimum absorbance shall be set at -0,05 and the maximum absorbance set at 1,00.

### 5.2.2.2 Fluorescence spectrophotometer

In measuring sample fluorescence with a fluorescence spectrophotometer, it is necessary to specify an excitation wavelength and wavelengths to start and end collection of the emission spectra. In choosing these wavelengths, consideration should be given to minimize the overlap region between the red edge of the excitation spectrum and blue edge of the emission spectrum where re-absorption of the fluorescence occurs. Evidence has shown that the OD in the overlap region is typically less than 0,05 to minimize re-absorption or inner-filter effects. In addition, the slit width on both the excitation and emission monochromators shall normally be set to the same value (see Table 1). In determining the slit width, there is a trade-off between signal intensity and peak resolution. It is recommended that the slit width be set to the minimum value that does not adversely affect signal-to-noise ratio. However, the spectral bandpass conditions (i.e., slit width multiplied by the reciprocal linear dispersion of the monochromator) shall remain invariant for the measurement of the sample and reference material. Other spectrophotometer properties such as photomultiplier tube (PMT) voltage shall also be the same for sample and reference materials.

Since fluorescence measurements are typically carried out over a narrower spectral region than absorbance measurements, different pre-determined acquisition protocols can be programmed into many instruments. Representative values from three methods, “Green QY method”, “Red QY method – high QY”, and “Red QY method – low QY” are provided in Table 1. In this example, QY stands for quantum yield. Different methods (and associated fluorescent material standards) would be required for other spectral regions of interest.

**Table 1 – Example fluorescence methods for relative measurements**

	Green QY method	Red QY method – high QY	Red QY method – low QY
Excitation	465 nm	540 nm	530 nm
Start collection	470 nm	545 nm	540 nm
End collection	700 nm	800 nm	850 nm
Excitation slit	2,5 nm	2,5 nm	2,5 nm
Emission slit	2,5 nm	2,5 nm	2,5 nm
PMT detector voltage	Medium	Medium	High

## 5.3 Calibration

### 5.3.1 General

Fluorescent materials with well characterized quantum efficiencies shall be used as calibration standards for relative measurements of solutions. In choosing a reference material, it is important that the excitation wavelength of the reference material be similar to the



expected excitation wavelength of the sample in the intended application. It is also important that the quantum efficiency of the reference material used in relative quantum efficiency measurements be equal to or greater than the expected value for the samples undergoing test. For SSL applications, the excitation wavelength often resides between 440 nm and 470 nm, although other excitation wavelengths may be used. The emission wavelength of the standard should also be similar to that of the luminescent nanomaterials sample. A list of potential reference materials may be found in reference [8] and other sources. Depending upon the spectral region of interest, multiple fluorescent materials may be required to provide accurate calibration. Examples of possible quantum efficiency calibration standards for relative measurements are provided in Table 2. Calibration standards for other wavelengths of interest can be found in reference [8].

**Table 2 – Suggested calibration standards for relative quantum efficiency measurements of luminescent nanoparticle solutions**

Fluorescent standard	Solvent	Excitation wavelength (nm)	Emission wavelength range (nm)	Method used	Quantum efficiency	Reference
Rhodamine 560	Ethanol	465	470 – 700	Green	0,92	10
Cresyl Violet	Methanol	540	540 – 850	Red	0,54	8,11
Rhodamine 101	Ethanol	465, 540	450 – 750	Green, red	1,00	8,12

### 5.3.2 Calibration standard – preparation

#### 5.3.2.1 Concentrated stock solution

Using a microbalance, weigh out approximately 2 mg of the fluorescent calibration standard in a 20 ml vial. Dissolve the dye in 10 ml of the appropriate solvent to create a concentrated stock solution of the calibration standard.

#### 5.3.2.2 Dilute stock solution

Remove 2 ml of the concentrated stock solution via syringe and place it into a 20 ml vial. Dilute the solution with an additional 8 ml of original solvent to create the dilute stock solution of the calibration standard.

### 5.3.3 Calibration standard – test measurements

#### 5.3.3.1 Initial measurement

Remove 2,5 ml of solvent and place into a quartz cuvette. Then run a baseline in the UV-Vis spectrophotometer.

Using a microsyringe, add 100  $\mu\text{L}$  of the calibration standard dilute stock solution to the cuvette and mix well.

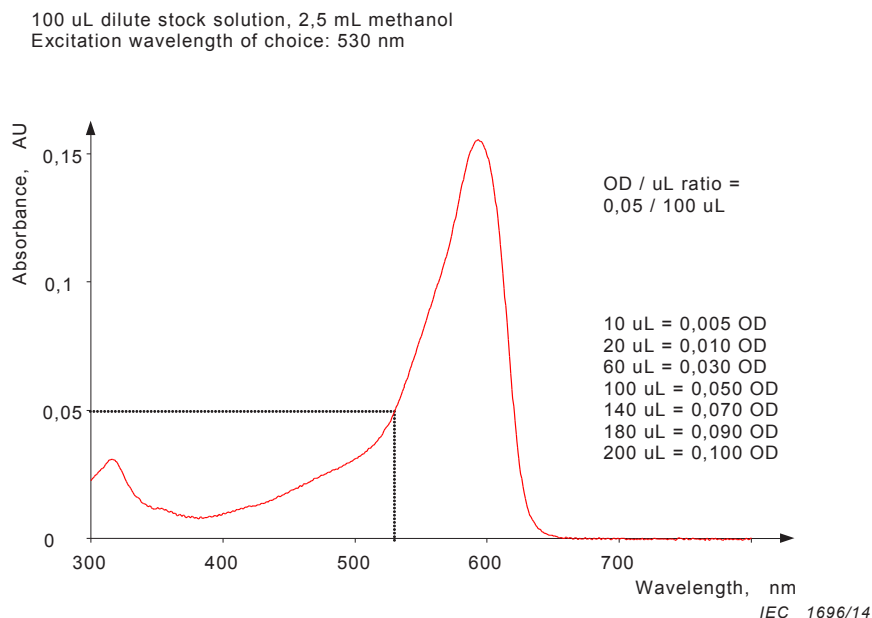
Take an absorbance measurement on the UV-Vis spectrophotometer and note the optical density (OD) at the excitation wavelength of choice.

#### 5.3.3.2 Maximum concentration measurements

Divide the noted OD by 100 in order to calculate an OD/ $\mu\text{L}$  stock solution ratio. With this number, concentrate or dilute the quartz cuvette solution to the point where the OD at the excitation wavelength is 0,05 (see Figure 1).

Check this calculation by taking an absorbance measurement on the spectrophotometer.

Using the methods described in 5.2.2.2, take a measurement using the fluorescence spectrophotometer. This will ensure that the maximum concentration does not produce a non-linear response, such as saturation, in the detector of the fluorescence spectrophotometer. If this is occurring, then the method parameters must be adjusted.



**Figure 1 – Sample absorbance spectrum of cresyl violet – example calculations**

## 5.4 Experimental procedure

### 5.4.1 Calibration standard – experimental measurements

#### 5.4.1.1 Obtaining a baseline

Remove 2,5 ml of the solvent used for the standard reference material and place into a quartz cuvette. Measure a baseline in the UV-Vis spectrophotometer.

#### 5.4.1.2 Varied concentration measurements

Using the OD/ $\mu\text{L}$  stock solution ratio described in 5.3.3.2, calculate the  $\mu\text{L}$  of standard dilute stock solution needed to obtain an absorbance of 0,001, 0,003, 0,005, 0,01, 0,03, and 0,05, at the excitation wavelength of choice (see Figure 1). These absorbances and the corresponding integrated emission intensities will be used to create the calibration curve for determining relative quantum efficiency.

NOTE The OD (i.e., absorbance) should not exceed 0,05 due to non-linear behaviour in the Beer-Lambert law, including re-absorption effects, associated with higher concentrations.

Add the appropriate initial amount of dilute stock solution to the solvent-containing cuvette and take measurements in the UV-Vis spectrophotometer and fluorescence spectrophotometer.

Add the appropriate second amount of stock solution to the cuvette.

Repeat the measurements for each additional amount of the standard stock solution added.

### 5.4.1.3 Data correction

To ensure accurate data analysis, open all of the emission spectra taken using the fluorescence spectrophotometer and multiply each by the “Correction Lamp” file obtained from a calibrated optical radiation source. The “Correction Lamp” file corresponds to the spectrophotometer detector response as a function of wavelength. The file should either be provided by the manufacturer or generated for a given spectrophotometer using a tungsten halogen calibration optical radiation source. As described elsewhere [9], other calibration methods, such as calibrated reference detectors, may also be used. In those instances, appropriate calibration corrections should be applied.

Save each corrected spectrum into a spreadsheet format. Calculate the total integrated peak area over the corrected emission peak.

### 5.4.1.4 Data input and calibration curve plot

NOTE The format described is based on the use of Microsoft Excel®<sup>2</sup>.

Using spreadsheet software, assign columns for absorbance (at the appropriate excitation wavelength) and for integrated fluorescence intensity. Input all of the data collected from the measurements.

Plot the data for the fluorescent reference standard with absorbance on the x-axis and integrated fluorescence intensity on the y-axis.

Create a linear regression trend line from the data with the intercept set to 0. Display the equation and R-squared value on the chart. This plot is the calibration curve associated with a specific fluorescent reference standard and similar plots must be repeated for each standard. The slope of this plot will be used in determining the relative quantum efficiency of the luminescent nanoparticle solution. From a historical log of previous slope values for a given standard, mean values and standard deviations can be calculated. Compare the slope obtained from the current linear regression to the values from the historical log and then determine whether the new reading differs from the historical mean by more than three standard deviations. If this value is more than three standard deviations from the historical log mean, then the calibration procedure shall be repeated.

In order to compare slope values of a calibration standard reference material, the methods used to collect the data should be identical – this includes excitation wavelength, slit width, collection start and end points, PMT detector voltage and the quantum efficiency fluorescent reference standard being used.

According to standard statistical process control rules, a deviation larger than three standard deviations implies that the spectrophotometer is out of control. The reason for the out of control condition must be investigated further and corrective action taken.

## 5.4.2 Luminescent nanoparticle sample – Experimental measurements

### 5.4.2.1 Obtaining a baseline

Remove 2,5 ml of solvent used for the luminescent nanoparticle sample and place into a quartz cuvette. Measure a baseline in the UV-Vis spectrophotometer.

### 5.4.2.2 Sample measurement – Single point measurement

Measure the absorbance of the nanoparticle sample using the UV-Vis spectrophotometer. If the sample absorbance at the excitation wavelength of interest exceeds 0,05, dilute with

<sup>2</sup> Microsoft Excel® is the registered trademark of a product supplied by Microsoft Corporation. This information is given for the convenience of users of this standard and does not constitute an endorsement by IEC of the product named. Equivalent products may be used if they can be shown to lead to the same results.

additional solvent until absorbance is below 0,05. The optimal OD range for the sample is between 0,03 and 0,05.

Record the sample absorbance using the UV-Vis spectrophotometer and measure the emission spectrum in the fluorescence spectrophotometer. Apply all data corrections as necessary (5.4.1.3) and calculate the total integrated peak area of the corrected emission peak (5.4.1.4). Repeat this procedure for other samples if necessary.

#### 5.4.2.3 Quantum efficiency calculation – Single point measurement

Quantum efficiencies of luminescent nanoparticles are calculated according to the format in Table 3.

**Table 3 – Spreadsheet format for quantum efficiency data comparisons**

A	B	C	D
Absorbance of sample at __ nm	Corrected integrated fluorescence intensity	Slope of standard reference material (e.g., dye)	Quantum efficiency calculation

Input the data for columns A and B. For column C, enter in the slope calculated from the standard fluorescent dye calibration curve measurements (see 5.4.1.4). For column D, enter the following equation:

$$D_i = (QE\ Standard * B_i * (Ref.\ Index\ Sample)^2) / (A_i * C_i * (Ref.\ Index\ Standard)^2)$$

where:

$A_i, B_i, C_i, D_i =$  entries in the spreadsheet cells for columns A, B, C, D, respectively, and row number  $i$  (i.e.,  $i = 1, 2, 3$ , etc.)

$QE\ Standard =$  quantum efficiency of the calibration standard reference material used

$Ref.\ Index\ Sample =$  refractive index of the solvent used with the sample

$Ref.\ Index\ Standard =$  refractive index of the solvent used to dissolve the standard dye

Test the quantum efficiency spreadsheet by measuring against other fluorescent standards of known quantum efficiency calibration standard dyes.

The methods used in both the standard dye and luminescent nanoparticle data collection shall be identical. This includes excitation wavelength, slit width, collection start and end points, and PMT detector voltage.

#### 5.4.2.4 Sample measurement – Full linear regression

Repeat the procedure in 5.4.2.2 over an OD range similar to that used to generate the calibration standard data (e.g. 0,001, 0,003, 0,005, 0,01, 0,03, and 0,05 OD; 5.4.1.2). For each sample, record the absorbance using the UV-Vis spectrophotometer and measure the emission spectrum in the fluorescence spectrophotometer. Apply all data corrections as necessary (5.4.1.3) and calculate the total integrated peak area of the corrected emission peak (5.4.1.4). Repeat this procedure for other nanoparticle samples if necessary.

### 5.4.2.5 Quantum efficiency calculation – Full linear regression

Using spreadsheet software, assign columns for absorbance (at the appropriate excitation wavelength) and for integrated fluorescence signal, typically in counts per second or equivalent units. Input all of the data collected from the measurements.

NOTE The format described is based on the use of Microsoft Excel®.

Plot the nanoparticle data with absorbance on the x-axis and integrated fluorescence intensity on the y-axis.

Create a linear regression trend line from the data, set the intercept to 0, and display the equation and R-squared value on the chart. The slope of this plot will be used to calculate the relative quantum efficiency of the luminescent nanoparticle solution as shown in Table 4.

**Table 4 – Spreadsheet format for quantum efficiency data comparisons**

A	B	C
Slope of nanoparticle sample (e.g., QDs)	Slope of standard reference material (e.g., dye)	Quantum efficiency of nanoparticle solution

Input the data for columns A and B. For column C, enter the following equation:

$$C_i = QE_{Standard} * (A_i / B_i) * (Ref. Index Sample)^2 / (Ref. Index Standard)^2$$

where:

$A_i, B_i, C_i =$  entries in the spreadsheet cells for columns A, B, C, respectively, and row number  $i$  (i.e.,  $i = 1, 2, 3$ , etc.)

$QE_{standard} =$  quantum efficiency of the calibration standard reference material used

$Ref. Index Sample =$  refractive index of the solvent used with the sample

$Ref. Index Standard =$  refractive index of the solvent used to dissolve the standard dye

The methods used in both the standard dye and luminescent nanoparticle data collection shall be identical – this includes excitation wavelength, slit width, collection start and end points, and PMT detector voltage.

## 6 Measurement of absolute quantum efficiency of nanomaterials

### 6.1 General

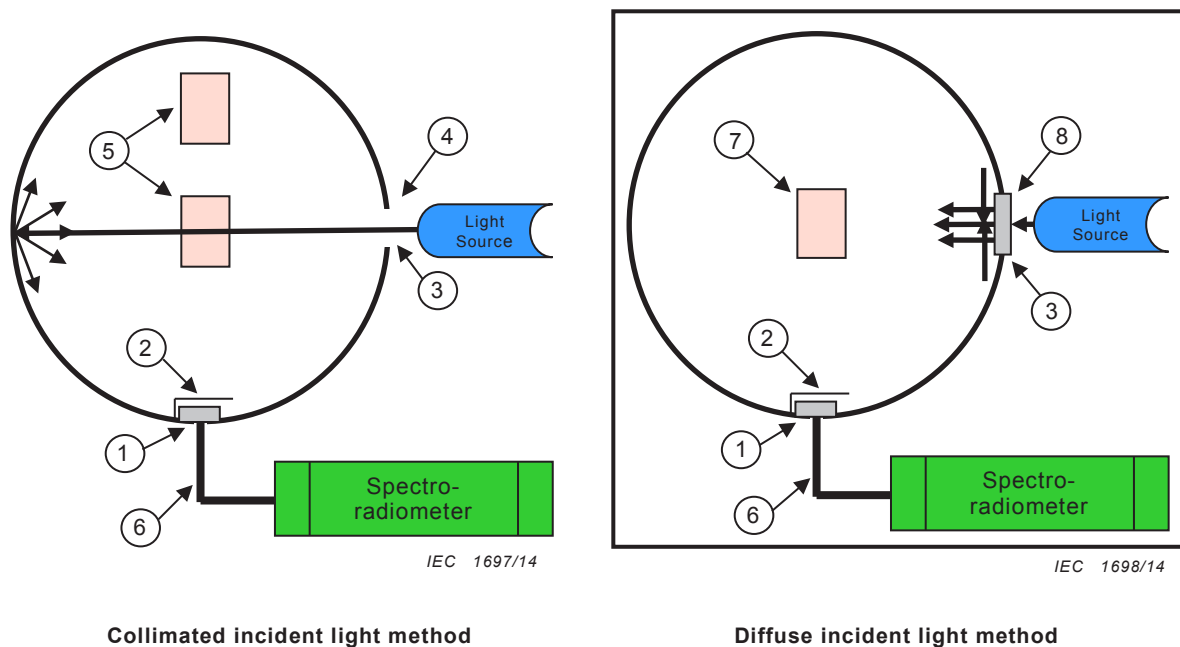
Absolute measurement techniques determine the quantum efficiency in terms of fundamental standards of mass, time, and distance. Reference standards traceable to base or derived SI units (e.g., NIST-traceable standard reference materials) are typically used for calibration in absolute measurements. This type of measurement can be performed on both solid and liquid samples.

There are two methods for measuring the absolute quantum efficiency of luminescent nanomaterials described in this document. The collimated incident light method is described in 6.5.1, while the diffuse incident light method is described in 6.5.2. A comparison of the two methods is provided in Table 5.

**Table 5 – Comparison of methods for measuring the absolute quantum efficiency of luminescent nanoparticles**

	<b>Collimated incident light</b>	<b>Diffuse incident light</b>
Required equipment	See Figure 2 and 6.2	See Figure 2 and 6.2
Number of measurements	Three	Two
Values used in calculations	Photon flux (1/s)	Spectral radiant flux (W/nm)
Accuracy	Highest	Good
Speed	Good	Fastest

Absolute measurements of the quantum efficiency of both liquid and solid samples can be performed using either a collimated incident light method or a diffuse incident light method. The equipment for both methods is very similar and the experimental set-ups are given in Figure 2.



- |            |                           |
|------------|---------------------------|
| 1 Port 1   | 5 Movable sample position |
| 2 Baffle   | 6 Fibre optic cable       |
| 3 Port 2   | 7 Sample                  |
| 4 Aperture | 8 Diffuser                |

**Figure 2 – Schematic of the test equipment configuration for both the collimated incident light and diffuse incident light methods**

## 6.2 Test equipment

- One integrating sphere with the interior coated with a material exhibiting greater than 95 % diffuse reflectance. In selecting an integrating sphere to performing these tests, it is critical that a sphere of appropriate size is chosen so that uniform light diffusion is achieved. Typically, this requires that the diameter of the sphere be at least three times larger than the longest dimension of the sample being tested. In general, choosing a larger sphere over a smaller sphere is advisable, although if the sphere is too large, there can be an undesired reduction in radiance striking the detector. In most applications, a sphere with a diameter of 10 cm or larger is sufficient. The sphere should contain a removable sample holder and at least two equatorial ports. In choosing the size of these ports, it is critical that no more than 5 % of the total sphere surface area be consumed by the ports. Guidelines on sphere diameters and port sizing can be found in reference [14].

The sample holder places the sample inside the sphere, and is coated with the same high diffuse reflectance material as the sphere. For the collimated incident light method, the sample holder should allow for moving the sample into and away from the collimated incident light beam. For the diffuse incident light method, there is no need to move the sample into and away from the incident light beam as irradiation occurs from a diffuse source only.

- Detector and light source ports meeting the following requirements:

The detector port (Port 1 in figure 2) shall have a light baffle of sufficient size as to block direct illumination of the detector by the light source. This port is covered with an adapter (typically a SMA connector) that mates with a fibre optic cable external to the sphere. In front of the adapter is placed a high transmittance light diffuser with near-Lambertian characteristics to ensure wide angle light collection.

The excitation light source port (Port 2 in figure 2) shall consist of a small aperture (typically less than 1,27 cm) through which light from the excitation source is introduced. For the collimated incident light method, the light source is introduced directly through this aperture without additional modification. For the diffuse incident light method, a high transmittance light diffuser with near-Lambertian characteristics is placed across the aperture to diffuse the excitation light source entering the sphere.

- Spectroradiometer capable of accurately measuring radiation intensity over the wavelengths of interest, typically between 350 nm and 900 nm. The spectroradiometer contains a grating blazed to provide optimal detection over the desired wavelength range. Various optical elements such as lenses and filters may also be incorporated into the spectroradiometer to improve collection efficiency and reduce stray light. The spectroradiometer is connected to the integrating sphere at Port 1 through an external fibre optic cable. Wavelength calibration of the spectroradiometer is verified at least annually using a light source of well-characterized emission wavelengths such as a mercury argon calibration source.

The use of a fibre optic cable is the preferred measurement method of coupling the spectroradiometer to the integrating sphere. However, in instances where the signal to noise ratio is acceptable, focusing optics with an f-number matched to the monochromator on the spectroradiometer may also be used at Port 1 instead of a fibre optic cable. This change in test procedure must be clearly described in the test report.

- Narrow-band light source chosen from one of the following:

Laser: the desired source with easiest control of wavelength, spectral width (FWHM) and beam shape (collimated narrow beam). This source allows for convenient delivery of light (particularly in the collimated incidence method described in 6.5.1), and its output stability can be controlled to high precision by temperature and current. The output can be pulsed or cw (continuous wave). Typically pulsing produces noise due to pulse-to-pulse intensity variation, the extent of which depends on the type of laser and the method of pulse creation. The latter can be modulated for better signal to noise ratio;

- LEDs: a convenient source due to low cost, wavelength selection and intensity (also spectral width depending on the source used). This source is relatively harder to deliver light in collimated incidence method, but very suitable for diffuse incidence method. For reliable operation, this source needs good temperature and current/voltage control. One must also be aware of the width of LED emission spectra and take care that the LED emission does not overlap with the emission spectra of the sample being analysed.
- Monochromatic discharge lamps: still a widespread and well-tested reliable option. However, their use is somewhat complicated in that their intensity per spectral interval can be relatively low due to the fact that the narrow bandpass reduces the throughput of the monochromator, and the intensity is further reduced by the finite f-number of the instrument and the beam not being collimated. This source is more suitable for diffuse incidence light method. In addition, this source may display some problems with output stability (both in pulsed and cw mode).
- Calibrated light source (e.g., spectral radiant flux or irradiance standard) calibrated for use in an integrating sphere. The output of the calibrated light source has been previously determined using traceable standards and a calibration file created. Calibration is carried out according to the procedure given in 6.3.



- Computer for collection and analyzing data.
- Optional accessories including short pass optical filters to control the peak shape of the excitation source, adapters for various light sources intended to be used with the sphere, and blanking plugs for unused ports on the integrating sphere.

NOTE See Annex A for general considerations regarding sample heating and excitation density.

### 6.3 Calibration

The calibration procedure for absolute measurements of luminescent nanoparticles requires that all test equipment components used in the measurement be calibrated simultaneously as a system. This includes the integrating sphere, sample holder, spectroradiometer, fibre optic cable, and other components.

In order to accurately calibrate the test equipment, a calibrated light source shall be used. Typically, the calibrated light source is a tungsten filament with a correlated colour temperature of roughly 3 000 K and covers the wavelength range of 350 nm to 2 000 nm. For wavelengths outside this range other standards should be used such as a deuterium lamp (200 nm to 400 nm). The calibrated light source can be introduced into the sphere either through the aperture in Port 2 or through a special fixture attached to Port 2.

A calibration file containing the spectral radiant flux of the standard (typically in W/nm) measured relative to a traceable standard is used to calibrate the test equipment as a whole. The calibrated light source is introduced into the test equipment and the spectral radiant flux ( $\Phi_{\text{obs}}(\lambda)$ ) measured. In general, the acquisition time of the spectroradiometer is set to obtain the highest practical value of  $\Phi_{\text{obs}}(\lambda)$  without causing saturation or other non-linear response of the detector on the spectroradiometer. This will ensure the highest sensitivity for the calibration measurement and any sample measurements.

The observed spectral radiant flux ( $\Phi_{\text{obs}}(\lambda)$ ) is compared with the calibration file at each wavelength to develop a correction factor ( $C(\lambda)$ ). The absolute spectral radiant flux ( $\Phi_{\text{ab}}(\lambda)$ ) of the standard for each wavelength is the product of  $C(\lambda)$  and  $\Phi_{\text{obs}}(\lambda)$ .

$$\Phi_{\text{ab}}(\lambda) = C(\lambda) \times \Phi_{\text{obs}}(\lambda)$$

The correction factors ( $C(\lambda)$ ) are used to correct values measured under identical experimental conditions for various samples.

### 6.4 Sample preparation

#### 6.4.1 General

The absolute measurement of quantum efficiency can be performed on either solution or solid-state samples. The sample preparation requirements for each are given in this subclause.

#### 6.4.2 Liquid samples

##### 6.4.2.1 Concentrated stock solution

Using a microbalance, weigh out a desired amount of the sample and dilute with an appropriate solvent to create a concentrated stock solution.

##### 6.4.2.2 Dilute stock solution

Remove 2 ml of the concentrated stock solution via syringe and place it into a 20 ml vial. Dilute the solution with an additional 8 ml of original solvent.



For absolute measurements in integrating spheres, the smallest possible solution volume should be used. It is necessary to specify the concentration of the luminescent material to provide the proper context for the measurement.

### 6.4.3 Solid state samples

Solid state samples can be prepared by mixing the quantum dot ( QD) or other luminescent material with a user-preferred matrix material such as silicone / epoxy in a suitable weight ratio and allowing for solidification/ hardening under controlled conditions. The mix may be clad by transparent packaging to prevent ambient elements from deteriorating the luminescent nanoparticles. The sample volume should be chosen in the preferred range to provide an accurate measurement of quantum efficiency. If necessary, the sample can be diluted with white nonfluorescent diffusely reflecting material such as pressed barium sulphate powder or sintered polytetrafluorethylene powder. Sample volume and the amount of dilution will depend on the concentration of luminescent nanoparticles as well as the dynamic range of the detector and size of integrating sphere to be used.

One possible configuration for measuring solid samples is to place a drop of uncured QD or other luminescent nanoparticle mix in a transparent organic matrix between two glass slides. Spacers can be used to keep glass slides apart during subsequent cure.

## 6.5 Test procedure

### 6.5.1 Collimated incident light method

The collimated incident light method is an absolute measurement of the quantum efficiency of luminescent nanomaterials in either liquid- or solid-phase materials. In this method, a collimated light beam is introduced into the integrating sphere and used as the primary excitation source. Additional details on this test method are found elsewhere [15].

After calibration of the test equipment, the calibrated light source (e.g., spectral radiant flux standard) is replaced with the desired excitation light source (e.g., laser, LED, or monochromated discharge lamp) as shown in Figure 2. The source must be collimated and introduced directly into the integrating sphere through the aperture at Port 2 in order to use this method. The beam divergence must be minimized so that the beam size introduced into the integrating sphere and striking the sample is at least 50 % smaller than the sample itself.

In the collimated incident light method, the sample holder used on the integrating sphere must have the ability to move the sample into and out of the direct path of the incident beam as shown in Figure 2. In this method, three different measurements are taken for each sample:

- Experiment A. Background measurement with no sample in the integrating sphere.
- Experiment B. Sample in the integrating sphere, but moved out of the collimated incident light so that the incident light beam strikes the walls of the integrating sphere first and only diffuse radiation strikes the sample.
- Experiment C. Sample in the integrating sphere and positioned so that the collimated incident light beam directly illuminates the sample and the sample is positioned so that any reflected light strikes the walls of the integrating sphere instead of passing back through the entrance.

In performing the collimated incident light method, it is essential that all calculations be performed on values in units proportional to photons per second. If the spectroradiometer attached to the integrating sphere has been calibrated for spectral radiant flux in units of W/nm, these values can be readily converted into a photon flux (in units of 1/second). The procedure for this conversion is as follows:

The radiant energy of a photon is given by the equation

$$Q = hc/\lambda$$

Where:

$Q$  = photon energy in joules (J)

$h$  = Planck's constant ( $6.626 \times 10^{-34}$  joules second (J s))

$c$  = speed of light ( $3 \times 10^8$  metres/second (m/s))

$\lambda$  = wavelength (in metres)

If the wavelength is expressed in nanometres (nm), this equation reduces to

$$Q_{\lambda} = 1,99 \cdot 10^{-16} / \lambda$$

If more than one photon is present at a specific wavelength, then the total radiant energy at that wavelength is the product of the number of photons ( $n$ ) and the photon radiant energy.

$$Q_{\text{total}} = nQ_{\lambda} = n(1,99 \cdot 10^{-16} / \lambda)$$

Where:

$n$  = number of photons

$\lambda$  = wavelength (in nm)

From this equation, a relationship for the number of photons can be derived:

$$n = (5,03 \cdot 10^{15}) Q_{\text{total}} \lambda$$

Photon flux (in units of 1/s) is obtained by substituting the photon radiant flux ( $\Phi$ ) (in units of watts or joules/second) for photon energy. The expression for photon flux then becomes:

$$\text{Photon flux} = \frac{\text{photons}}{\text{second}} = (5,03 \cdot 10^{15}) \Phi \lambda$$

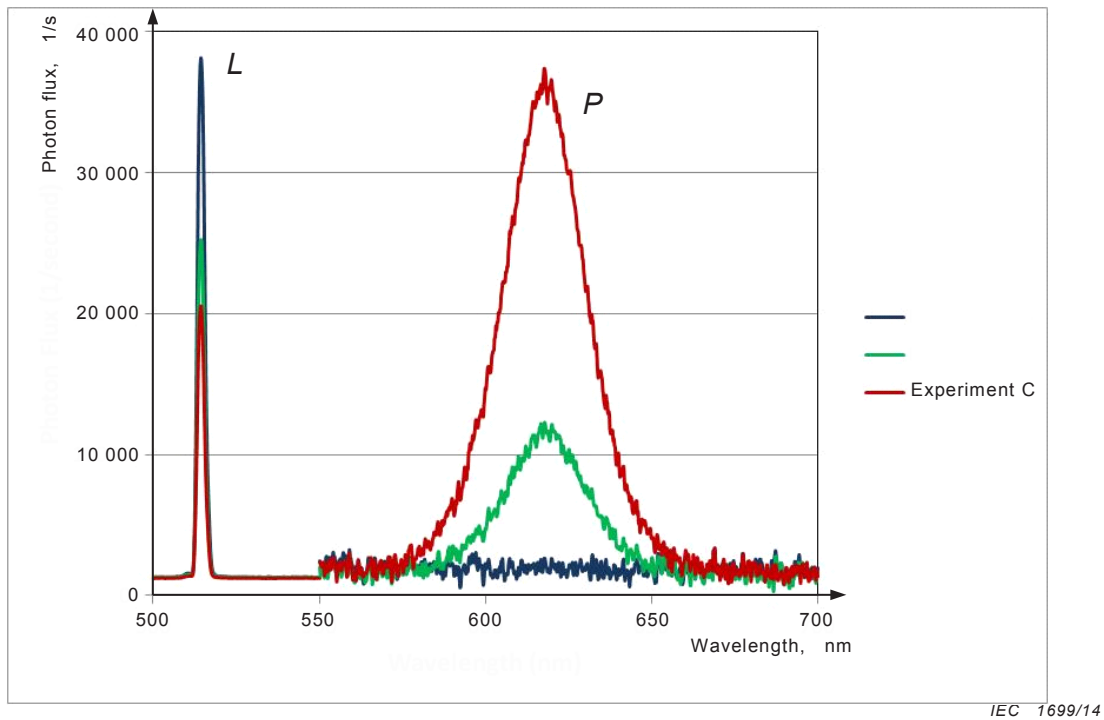
Where:

$\Phi$  = photon radiant flux (W)

$\lambda$  = wavelength (nm)

Consequently, the product of wavelength and photon radiant flux will provide a value proportional to the number of photons per second.

The spectral power distribution can be converted into a graph whose y-axis is proportional to the number of photons per second within a given wavelength interval by multiplying wavelength by the spectral radiant flux at that wavelength. A typical example is shown in Figure 3.



- L* Source
- P* Emission

**Figure 3 – Sample spectrum for collimated incident light method**

With no sample in the integrating sphere (Experiment A), the background photon flux is measured. This instrument background signal is largely due to stray light from parasitic scattering within the sphere and needs to be subtracted for all subsequent measurements.

Place the sample in the integrating sphere directly in the path of the incident beam (Experiment C). Since the light beam is collimated, it will strike the sample at a normal incidence angle when the sample is placed directly into the beam (Experiment C). A fraction,  $A$ , of this incident light will be absorbed by the sample and the remainder will be either transmitted or reflected by the sample. This transmitted and reflected light will in turn strike the walls of the integrating sphere and be diffusely scattered toward the sample. Any light emitted by the sample will also be diffusely scattered by the integrating sphere. Hence, in the collimated incident light method, the sample receives principal radiation from the collimated light source (angle of incidence  $\sim 0^\circ$ ) and additional radiation at all angles of incidence from the light diffusely scattered by the integrating sphere

If the sample is placed in the integrating sphere, but away from the incident collimated light, the sample will be irradiated only by diffusely scattered radiation at all angles of incidence (Experiment B). A fraction,  $\mu$ , of this scattered light is absorbed by the sample, and the remainder is either transmitted or reflected. This transmitted and reflected light will in turn strike the walls of the integrating sphere and again be diffusely scattered toward the sample. Any light emitted by the sample will also be diffusely scattered by the integrating sphere.

The spectrum from each of the three measurements is analyzed and the source and photoluminescent emission peaks identified. After subtracting the instrument background, the area under each identified peak is obtained by integration and provides a value proportional to the number of photons per second within a given wavelength interval. The area under the source peak is referred to as  $L$  and provides a measure of the source light that is not absorbed. The area under the emission peak is referred to as  $P$  and provides a measure of the emitted light. Additional corrections such as stray light compensation [16] and self-

absorption [17] may also be applied. At a minimum, the analyzed spectrum will contain the following values:

$L_a$  – source peak area with no sample in the integrating sphere (Experiment A)

$L_b$  – source peak area with sample in the integrating sphere but diffusely illuminated only (Experiment B)

$L_c$  – source peak area with sample in the integrating sphere and illuminated by collimated incident light and diffusely scattered light (Experiment C)

$P_b$  – photoluminescence emission peak area with sample in the integrating sphere but diffusely illuminated only (Experiment B)

$P_c$  – photoluminescence emission peak area with sample in the integrating sphere and illuminated by collimated incident light and diffusely scattered light (Experiment C)

All values of  $L$  and  $P$  shall be converted to units proportional to photons per second using the procedures described above in 6.5.1.

From these parameters, the fraction of incident light that is absorbed ( $A$ ) and quantum efficiency ( $\eta$ ) can be calculated using the formulas below (method described in more detail elsewhere [15]):

$$A = (1 - L_c/L_b)$$

$$\eta = (P_c - (1 - A)P_b)/L_a A$$

This expression can also be written as:

$$\eta = \frac{P_c L_b - P_b L_c}{L_a (L_b - L_c)}$$

### 6.5.2 Diffuse incident light method

The diffuse incident light method allows the measurement of the quantum efficiency of luminescent nanomaterials in either liquid- or solid-phase materials. This method is an absolute measurement of quantum efficiency and uses a diffuse light beam that strikes the samples at all angles of incidence as the excitation source.

After calibration of the test equipment, the calibrated light source is replaced with a light source (e.g., laser, LED, or monochromated discharge lamp) and a light diffuser as shown in Figure 2. The light diffuser acts to introduce light into the sphere at diffuse angles and provide diffuse illumination of the sample. Additional details relevant to the diffuse incident light method are found elsewhere [18].

In the diffuse incident light method, spectral radiant flux values in units of W/nm are used in all calculations, and the area under the observed line shapes, after removal of the background, is determined by integration to provide the source ( $L$ ) and emission ( $P$ ) radiant power. In the diffuse incident light method, only two measurements are taken to compute quantum efficiency ( $\eta$ ):

- Experiment A. A blank sample in the integrating sphere. The blank shall be representative of the form of the sample to be tested. Depending on the sample form, the blank may be an empty cuvette (for liquid samples measured in an equivalent cuvette), unfilled silicone matrix (for solid samples embedded in equivalent silicone material), uncoated substrate (for solid samples coated on to an equivalent substrate), or other forms. This measurement provides  $L_A$ , the source peak with only the blank sample in the sphere.

Experiment B. Sample to be tested is placed in the integrating sphere and subjected to illumination from a diffuse light source. This measurement provides  $L_B$  (from the source peak) and  $P_B$  (from the emission peak).

The spectral power distribution of the excitation light source shall be recorded with no sample using the same acquisition parameters as set in the calibration step. The integral of this spectrum is the optical power ( $L_{ex}$ ) of the excitation light introduced into the sphere. Likewise, the background spectrum ( $L_{back}$ ) shall be recorded with the light source switched off. The total optical power ( $L_{total}$ ) input into the sphere can be calculated as the difference between  $L_{ex}$  and  $L_{back}$ .

$$L_{total} = L_{ex} - L_{back}$$

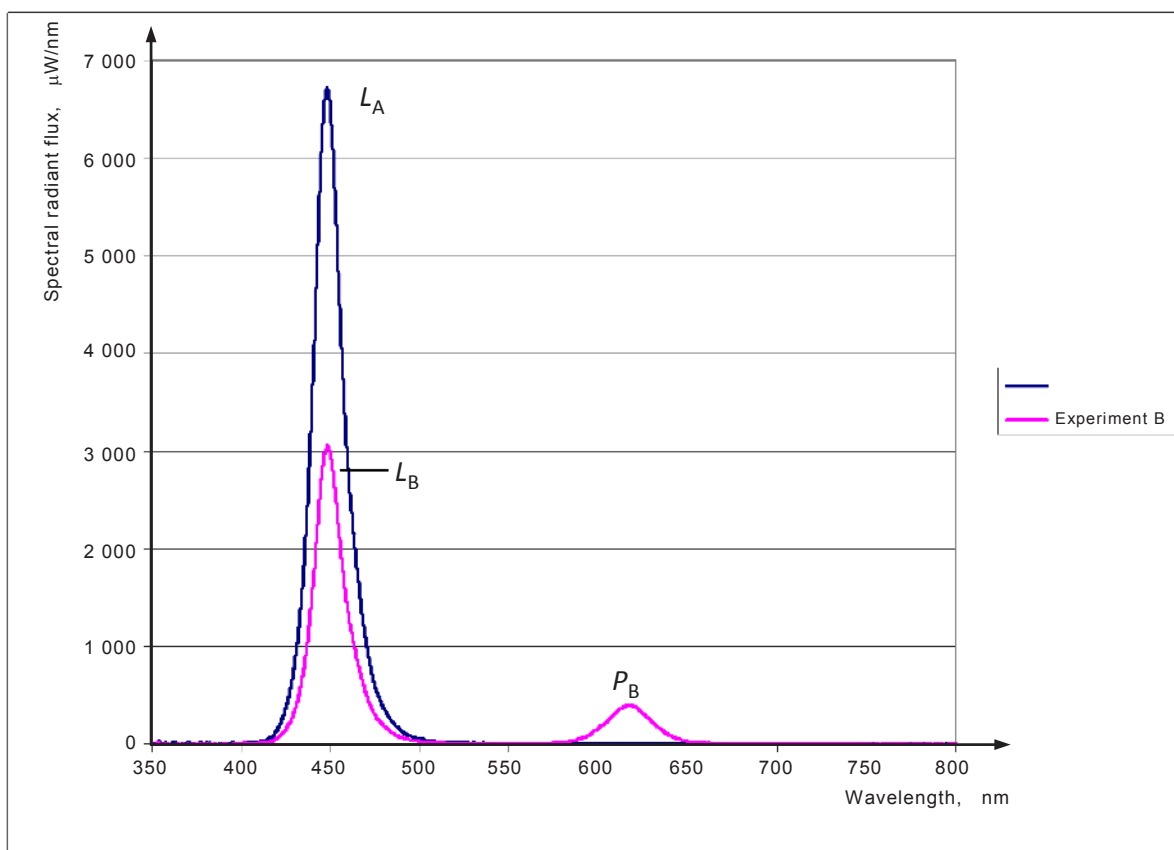
In Experiment A, a blank sample, of size corresponding to the sample to be tested, is placed into the holder on the integration sphere. The spectral power distribution for this blank sample is recorded at each wavelength using the same acquisition parameters as set in the calibration step. The difference in the integrated optical power of this spectrum ( $L_A$ ) and that recorded with no sample (i.e.,  $\Delta L = L_{total} - L_A$ ) is the amount of light absorbed by the blank. In order to keep this difference as low as possible, the use of coloured markings on the blank should be avoided.

The blank is removed from the sample holder and replaced with the sample prepared as described in 6.4. The spectral power distribution for the sample is recorded using the same acquisition parameters as set in the calibration step. The difference in the integrated optical power of this spectrum and that recorded for the blank sample contains information on the fraction of the light absorbed by the sample and its subsequent re-emission via fluorescence. These values are referred to as:

$L_B$  = source power with sample in integrating sphere and illuminated by diffuse radiation;

$P_B$  = photoluminescence emission power with sample in integrating sphere and illuminated by diffuse radiation.

A representative spectrum is shown in Figure 4. The blue trace represents the spectra of the sample blank, and the peak from the excitation source ( $L_A$ ) is visible at 470 nm. The red trace represents the spectrum obtained from a sample containing QDs. Both the unabsorbed source peak ( $L_B$ ) and the emission peak from the photoluminescent nanomaterials at roughly 620 nm ( $P_B$ ) are visible.



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**Figure 4 – Sample spectra for the diffuse incident light method**

Using this information, the quantum efficiency of the sample can be calculated. The change in the integral of the excitation peak between the blank ( $L_A$ ) and the sample ( $L_B$ ) provides the amount of the diffuse incident radiation power absorbed by the sample.

The integral of the emission peak ( $P_B$ ), after correcting for the background ( $P_{back}$ ), provides the amount of optical power emitted by the fluorescing QDs.

The power conversion efficiency (PCE) of the sample can be calculated as follows:

$$PCE = (P_B - P_{back}) / (L_A - L_B)$$

The PCE is proportional to the quantum efficiency through the wavelength of an emitted photon of average energy ( $\bar{\lambda}$ ) which shall be calculated for both the emission spectral power distribution ( $\bar{\lambda}_p$ ) in Experiment B and the excitation spectral power distribution ( $\bar{\lambda}_{LA}$ ) in Experiment A. In general, the photon of average energy can be calculated from the spectral radiant flux distribution ( $R(\lambda)$ ) as:

$$\bar{\lambda} = \int \lambda R(\lambda) d\lambda / \int R(\lambda) d\lambda$$

From these values, the quantum efficiency ( $\eta$ ) can be calculated:

$$\eta = PCE * (\bar{\lambda}_p) / \bar{\lambda}_{LA}$$

## 7 Uncertainty statement

Uncertainty of quantum efficiency measurements can vary widely depending on equipment, experimental conditions and laboratory personnel practices. Users of this standard are encouraged to reference IEC/ISO Guide 98-3 for guidance and other related online tools and literature [19].

In order to provide the proper context for the measurements, an estimate of uncertainty should be provided in the test report. Identify in order of significance the important sources of uncertainty (Type A and Type B) for the various test methods used in this standard. The report should include estimates of both the Type A and Type B uncertainties and how these are combined to give the overall expanded measurement uncertainty.

The components of uncertainty will vary depending upon the quantum efficiency measurement technique employed (i.e., relevant or absolute test methods) and will change with any modification of the test procedure. Uncertainty estimates shall be reviewed whenever a change in the measurement process is made.

## 8 Test report

The test report shall include at a minimum, the following:

- date and individual/organization performing test;
- ambient conditions;
- physical state of matter;
- description of sample preparation;
- absorbance or optical density at excitation wavelength;
- test method used;
- equipment used (spectrophotometer or spectroradiometer wavelengths, sphere diameter, sample location during test, excitation introduction, other optical elements);
- calibration source and method including lamp wattage, lamp type, intensity distribution type – omni-directional/directional and its traceability for absolute measurements;
- excitation wavelength, source, power level, and peak shape;
- emission wavelength;
- spectral power distribution;
- quantum efficiency;
- estimates of uncertainty shall be given for each measurement parameter that influences the overall measurement uncertainty (e.g., excitation wavelength, emission wavelength, ambient conditions, calibration source, etc.). The test report shall also include a statement of overall measurement uncertainty for the quantum efficiency determination including the coverage factor and the confidence level.

## Annex A (informative)

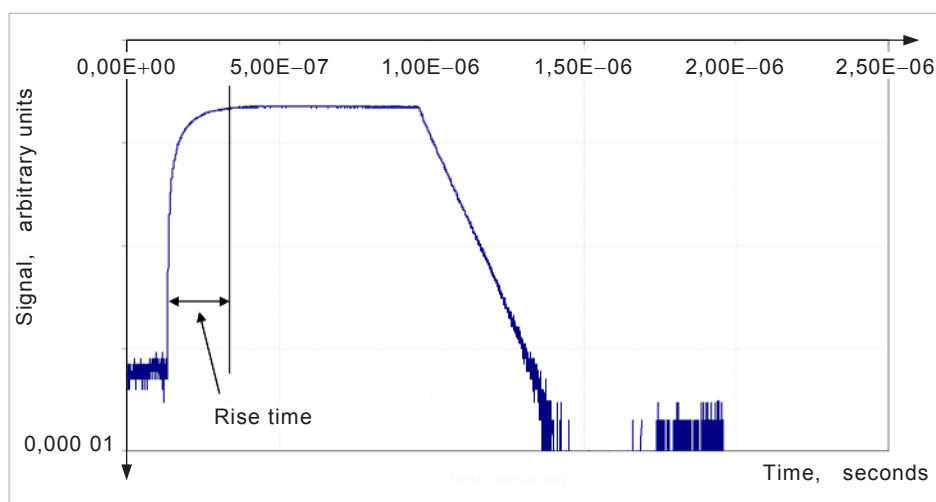
### Temperature quenching of quantum efficiency, light modulation considerations for avoiding sample heating, and achieving the best measurement conditions

#### A.1 Overview

The effect of quantum efficiency (QE) quenching due to temperature (TQE) is an important consideration for QE measurements. The heating of a sample is dependent on a variety of factors such as the energy difference between excitation and emission spectra (Stokes loss), the actual (but unknown) starting value of the QE of the material with no incident radiation (lower QE will automatically heat the sample more for the same excitation density), the host matrix in which the luminescent nanomaterials are suspended and the thermal coupling between the measured sample and the rest of the experimental setup, and finally, the provision for heat dissipation dependent on the setup itself. One is bound to encounter such effect if the QE is characterized as a function of excitation density. While this consideration may be addressed by a variety of hardware solutions, the following is an example of how TQE can be addressed by using a modulated light source such as a diode laser.

#### A.2 Addressing TQE

Diode lasers are attractive light sources due to the ease of optical beam management, output stability and the independent adjustment of pulse width and duty cycle. The limiting factor for the width of the pulse is the rise and the decay times of luminescence from the sample. The pulse width should be chosen to allow for the emission from a sample to saturate. Figure A.1 illustrates a YAG:Ce sample showing a luminescence rise time of approximately 0,25  $\mu\text{s}$ . It should be noted that the rise and fall time are dependent on the excitation density as well as the measurement setup and such check may be necessary for various excitation densities of interest. For example, if the purpose is to avoid heating altogether, then very short pulses or a low duty cycle have to be used. In general, the maximum heat deposited  $\Delta Q = \Delta t(\text{time}) \times P(\text{power})$  during the pulse will raise the temperature depending on the estimated specific heat capacity  $C$  and mass  $m$  of the material, as  $\Delta T = \Delta Q / mC$ . This can range from a fraction of degree to several degrees per pulse of heating above ambient temperature.



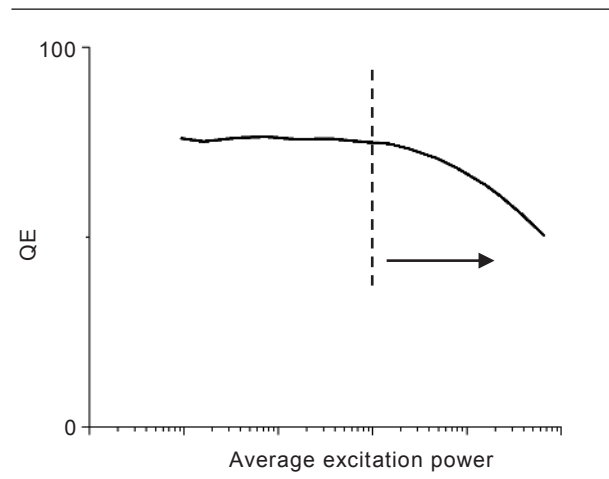
IEC 1701/14

Figure A.1 – Example of transient behaviour of luminescent material (YAG:Ce) under pulsed excitation



In this example, excitation pulse width is longer than the saturation time for luminescence signal. However, this may not reflect the conditions used in various user applications and therefore one may deliberately add heating without specifically knowing the exact effect of it, just measuring the compounded resultant QE expected from the material under user-defined circumstances.

The boundary conditions for the duty cycle are established by the dynamic response of the detector in the QE setup and sample heating. Figure A.2 illustrates a typical curve showing calculated QE as a function of the average excitation density. Here, a particular average excitation density may be achieved by varying pulse width and the duty cycle separately. Quantum efficiency is determined by using test procedure in 6.5. Similar curves can be constructed using a variety of duty cycle/pulse width combinations for various peak laser power levels. In the schematic in Figure A.2 for example, the dashed line indicates a region where the onset of heating occurs, usually accompanied by shift in emission spectra of QD sample. Therefore, the measurement of QE must be performed at excitation powers below this level. At high excitation, it is important to make sure that the detector is in its linear range as well as other physical effects responsible for inherent sub-linearity of the light output of most materials at high incident flux values are considered. Details on standardized methods for evaluating the linearity of fluorescence measuring instrumentation are found elsewhere [4,6].



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**Figure A.2 – Schematic diagram of variation of normalised QE with average excitation power and the preferred range of input power (indicated by vertical lines)**

NOTE An alternative to pulsed diode lasers is a temperature-stabilized continuous wave (cw) laser with an electronically controlled frequency modulation (chopping) wheel. This hardware combination allows one to access longer pulse widths and lower frequencies from sub-Hz to kHz range but not in an entirely independent manner. The advantage is improved signal-to-noise ratio compared to cw alone and riddance of pulse generation noise evident in non-solid state laser sources.

The physical mechanisms for such behaviour are described in literature [20, 21, 22] and depend on the nature of absorption which will determine the excitation volume. For example, excitation in the spectral range where there is high volume concentration of microscopic oscillators (such as fundamental / band gap absorption of the material) or high absorption coefficient due to other transitions results in very shallow absorption depth and hence in high excitation density. As far as these effects are concerned, the choice of measurement conditions should depend on whether one is interested in the intrinsic properties of the material or the properties that become evident in a particular application. A general guideline for finding the intrinsically best performance of the material is to use the lowest intensity without sacrificing signal-to-noise ratio in the data acquisition.

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<sup>3</sup> In preparation.





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