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Low cost 3D-printing used in an undergraduate project; an integrating sphere for measurement of photoluminescence quantum yield.

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Abstract

We report upon the exploitation of the latest 3D printing technologies to provide low-cost instrumentation solutions, for use in an undergraduate level final-year project. The project addresses prescient research issues in optoelectronics, which would otherwise be inaccessible to such undergraduate student projects. The experimental use of an integrating sphere in conjunction with a desktop spectrometer presents opportunities to use easily handled, low cost materials as a means to illustrate many areas of physics such as spectroscopy, lasers, optics, simple circuits, black body radiation and data gathering. Presented here is a 3rd year undergraduate physics project which developed a low cost (£25) method to manufacture an experimentally accurate integrating sphere by 3D printing. Details are given of both a homemade internal reflectance coating formulated from readily available materials, and a robust instrument calibration method using a tungsten bulb. The instrument is demonstrated to give accurate and reproducible experimental measurements of luminescence quantum yield of various semiconducting fluorophores, in excellent agreement with literature values.

1. Introduction

This paper reports and reflects upon the use of certain technological innovations in the planning and delivery of undergraduate physics student projects.

Final year student projects are a cornerstone of most undergraduate science degree courses [1]. In the Department of Physics at Aberystwyth University, students undertake major research-based projects, working in groups of one or two. These projects count for 40 credits or 1/3rd of the overall final year assessment [2]. The latest 3D printing technologies provide low-cost instrumentation solutions for optoelectronic materials characterisation, which would otherwise be inaccessible to such undergraduate student projects. This project also leaves a clear legacy, in terms of new apparatus, enhancing the scope of future projects.

Photoluminescent materials old and new have been extensively investigated since the first descriptive understanding of fluorescence by Sir George Stokes in 1852 [3]. In the modern world, luminescent materials are used in a wide variety of applications, ranging from advanced diagnostic markers in biomedicine, new mobile phones, TV's and computer tablets which have display screens that use organic semiconducting polymers to produce light emission [4], to simple highlighter pen inks. The efficiency of a fluorescent material is related to its internal photo-luminescent quantum yield (PLQY) [5]. The PLQY is simply the ratio of the number of photons emitted by the material to the number of photons absorbed (i.e. photons out / photons in) [6]. The PLQY of a material is also indirectly

related to its electroluminescence efficiency. So mobile phones, TVs and computer tablets use display materials that have a high PLQY because this reduces energy consumption [7].

Experiments to find the PLQY of film materials can be difficult to achieve because of problems in collecting all of the emitted light due to an angular anisotropy of emission. This difficulty can be overcome by using an integrating sphere to collect all of the emitted light [8,9]. The purpose of an integrating sphere is to spatially integrate radiant flux; by design, they are hollow spheres coated internally with a highly diffusely reflecting material. When a light source is placed inside the sphere the light output is redistributed isotropically over the whole of the internal surface, despite any angular preference of the initial emission [3,10,11]. This light can then be collected with a fibre-coupled spectrometer to determine the spectrum and intensity. Measurement of thin-film fluorescent materials using an integrating sphere was first developed by Greenham *et al* [8]. Their approach used a laser as an excitation source and made suitable corrections for the re-absorption of scattered light within the sphere. This technique was then further developed by deMello *et al* [9] and it is a variant of this method that is favoured in this report. A review of the measurement procedures and error analysis is provided by Leyre *et al* [12].

Commercial lab-grade integrating spheres are expensive; 100 mm diameter spheres with similar functionality to that proposed here typically cost several thousand pounds at present. To take absolute measurements, the sphere-spectrometer system also requires calibrating, usually to a National Institute of Standards and Technology (NIST) verified black-body light source, which further extends the cost well beyond most schools and undergraduate laboratories. Given existing access to a suitable CCD-coupled spectrometer and 3D printer, we present here a low cost (under £25) method to manufacture and calibrate an integrating sphere. The aim is to produce an experimentally robust and accurate instrument which presents opportunities to measure state-of-the-art photoluminescent material samples in a simple easily executed experiment, in order to calculate their PLQY. This provides opportunities to directly illustrate many areas of undergraduate physics including, optical spectroscopy, lasers, optics, simple circuits, black body radiation, and data gathering. For more ambitious students, projects involving detailed calibration of the sphere may be of benefit. The computer aided design (CAD) models and stereo lithography (STL) files for 3D printing, and the SciLab code for calculation, are available as supplementary information.

2. Method

2.1. Experiment Design of Integrating Sphere

As described in the introduction, the experimental method was first developed by deMello *et al* [9], and the schematic layout and physical set-up is as shown in Figure 1.

The body of the integrating sphere was CAD solid-modelled using 'Design Spark Mechanical', which is a freely available download from RS Components (Figure 1) [13]. The sphere was then manufactured using a Renkforce RF1000 3D printer [14]. The body is designed in two hemispheres, which are hinged together using two pins turned from PTFE plastic. The hemispheres have a light trap labyrinth at the mating faces, minimising any stray light entering the interior of the sphere. This allows data collection on samples to take place in a fully lit room. The side port, which allows the illuminating laser light to enter, was made large enough for a laser pointer to be held securely in place. It is important that the photo detector is not subject to direct illumination from any portion of the incident flux, so it is necessary to build a baffle arrangement into the sphere. The baffle is manufactured as a separate part, again using 3D printing, and is fitted into the upper half of the sphere, directly shielding the fibre optic cable port. The fibre optic cable can be connected to the sphere by a standard (SMA) fitting, which was screwed directly over the aperture in the top of the sphere.

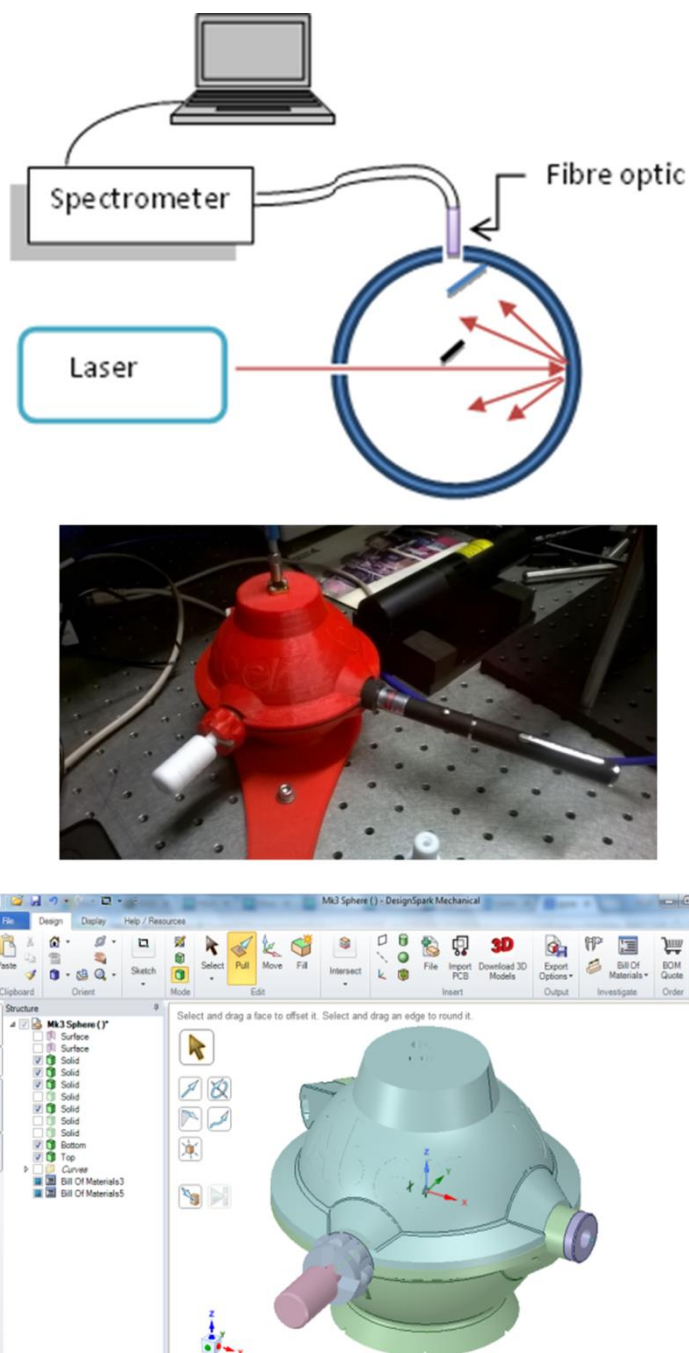


Figure 1. (Top) schematic of experimental set-up used, with a corresponding photograph of the main components in the middle image. (Bottom) shows a “screen shot” of the CAD model of the integrating sphere design.

2.2. Illuminating Laser

The illumination source used in the experiments was a Class 2 405 nm laser pointer with a power output of 0.5mW and hence safe for use by undergraduates following laser user training and appropriate supervision. This type of laser pointer is readily available for just a few pounds and has acceptable power stability for the purposes of these experiments [15]. It should be noted that the more common 635 nm ‘red’ pointers do not have sufficient photon energy to initiate fluorescence in many sample materials. For the measurement of Anthracene, a 365 nm ultra violet lamp was used (Thor Labs M365L2 LED 190 mW). This reduces self-absorption from the emission of Anthracene, part of which occurs at 400 to 425 nm complicating accurate calculation of PLQY values.

2.3. Sample Holder

The aim is to provide a convenient, simple and repeatable means of supporting the sample in the centre of the sphere, while enabling the two sample positions (Figure 2) to be easily achieved externally. The sample holder attaches to the sphere by means of a mounting boss which has a bayonet fitting, thus also providing a suitable light trap. This feature also allows easy removal and consistent positioning of each sample after re-mounting, and is designed to ensure that it can only be attached in one orientation. The mounting boss and the sample holder are sprung loaded to hold the sample in each of the two set up positions required. Finally, the sample holder is turned from PTFE with “music wire” bent to form a sprung holder for the individual samples.

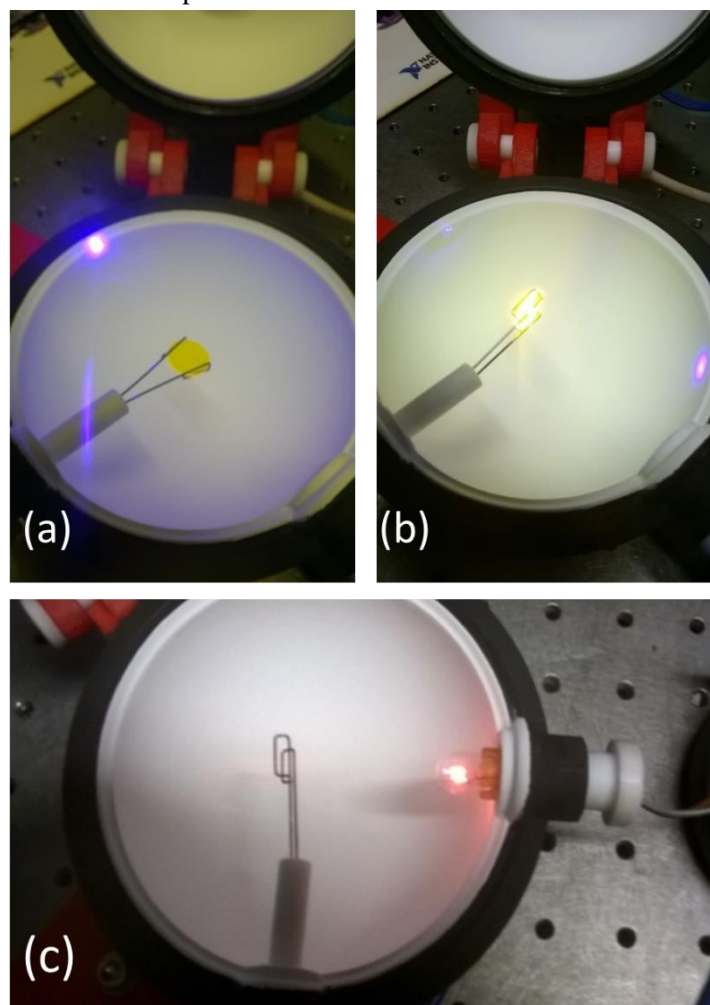


Figure 2. These images show the sample holder as positioned inside the two hemispheres of the integrating sphere. (a) Shows the sample indirectly illuminated (sample “out”), (b) shows the sample directly illuminated (sample “in”) with a $\lambda = 405$ nm laser pointer, (c) shows the Lucas 501 tungsten bulb (operating at low voltage) held in position within the sphere prior to calibration.

By angling the wire clips which hold the sample around 15° off-axis, two objectives are achieved. Firstly, when the sample is positioned into the laser light source (sample “in”), any reflected laser light is projected onto the surface of the sphere and not directly back towards the source. Secondly, an eccentric action is created, so that rotating the sample holder by 90° on its axis swings the sample clear of any direct illumination. Once the experiment is initially aligned, the sample holder and mounting are easily removed to facilitate the exchange of samples. Placing the sample in each of the two required positions is as simple as rotating the sample holder to one of the two indented positions on the mounting

boss. An internal spring and external pin both locks the holder in place in an indent and provides a visual external indicator of the sample position. This arrangement provides for a rapid method of data collection and a good level of repeatability in positioning. However, a simpler, more easily manufactured arrangement could be fashioned, depending on the type of sample material chosen and other classroom/laboratory factors.

2.4. Sphere Internal Coating

The raw interior surface of the 3D printed sphere was lightly sanded with P120 grit production paper to remove any raised imperfections and the worst of the striations from the printing process. The next step was to apply a plastic to paint adhesion promoter; U-pol S2003 was used in accordance with its data sheet. The next stage was to apply a surface filler (U-Pol S2020 HS Primer Filler) to allow the inner surface to be sanded to a smooth profile. Once dry, it was sanded with P320 grit paper to give a good key for the final internal reflectance coating. Readily available aerosol-based high build primer could be used, provided a number of carefully applied coats produced a suitable primer thickness, allowing it to be sanded smooth.

Because an important aim of the project was accessible cost, a homemade reflective coating was formulated. It comprised 500 grams of 99% purity Barium Sulphate, obtained at a cost of £8 from an online auction site, mixed with 1% by weight common Poly-Vinyl Acetate (PVA). This mixture was thinned for spraying using 50% to 60% by weight, de-ionised water. Application onto the inner surface of the sphere comprised of five wet-on-wet coats, followed by a further 10-15 dry dust coats to improve matting of the final surface. The reflectance spectrum of the homemade coating was measured and compared to the commercial product 'Avian-B', using a known >99% reflectance standard (Ocean Optics WS-1-SL) [16]. It may be thought that a standard domestic white paint might suffice, but they are however not particularly white or stable. They have a typical reflectance of 85-88%, compared with 90-95% for the homemade coating described above, and most suffer significant drop-off at the blue end of the spectrum, due to the use of titanium oxide as a pigment [17]. As the baffle, as described above, forms an integral part of the sphere interior, an identical reflective coating was also carefully applied to this component.

2.5. Calibration

In order to obtain experimentally accurate results, a spectral response calibration of the sphere/spectrometer system is necessary.

For any known photon flux, $f(\lambda)$, entering (or from within) the sphere, the spectral response as measured by the detector system (L_a) is the result of the instrument response function of the detector $R_{de}(\lambda)$:

$$L_a = f(\lambda) R_{de}(\lambda) \quad (1)$$

Calculation of the instrument response function, $R_{de}(\lambda)$, using the known irradiance of a calibration source, $f_{std}(\lambda)$, over the surface of the sphere, is the ratio of detected response $L_{std}(\lambda)$ to known photon flux:

$$R_{de}(\lambda) = \frac{L_{std}(\lambda)}{f_{std}(\lambda)} \quad (2)$$

This function can subsequently be applied to any gathered sample emission data, to produce a spectrum that is corrected for instrument response. Calibration to a source of known irradiance, $f_{std}(\lambda)$, was approached in two ways. The first is the method of Kosch and Harang [18], the theory of which

transforms a standard tungsten bulb into its equivalent blackbody radiator. Their model estimates a maximum error of around 15% compared to a fully certified NIST verified spectral irradiance lamp.

To facilitate this method, a bulb holder was turned from PTFE to support a standard Lucas 501 tungsten bulb within the body of the sphere as shown in Figure 2c. With the bulb in a holder within the sphere, a desktop power supply can be used to provide a known voltage (V_f) and measured current (I_f); firstly the resistance of the bulb (R_o) at room temperature (T_o) is measured as accurately as possible. In our case a Fluke 287 multi meter was used. Accuracy of the resistance measurement is critical to the process and further methods of improvement such as extrapolation from a range of voltage and current measurements should be considered. The operating resistance of the bulb can then be calculated as $R_f = V_f / I_f$, with the corresponding bulb spectrum being taken, which becomes our detected response, $L_{std}(\lambda)$. The next aim is to calculate the bulb filament operating temperature. With power supplied to the bulb, the resistance ratio is:

$$R(T_f) / R(T_o) = \rho(T_f) / \rho(T_o) \quad (3)$$

where ρ represents the value for Ohmic resistance of Tungsten. This value is low at room temperature but rises as temperature increases, and can be expressed by a second order polynomial for each of the two bulb temperatures.

$$\text{For } 200\text{K} < T_o < 400\text{K: } \rho(T_o) = 1.25 \cdot 10^{-6} T_o^2 + 0.0236 T_o - 1.57 \quad (\mu\Omega \text{ cm}) \quad (4)$$

$$\text{For } 1200\text{K} < T_f < 2500\text{K: } \rho(T_f) = 1.79 \cdot 10^{-6} T_f^2 + 0.0264 T_f - 3.25 \quad (\mu\Omega \text{ cm}) \quad (5)$$

Re-arranging equation 3 and using equation 5, we can establish a temperature of the bulb filament when the sample spectrum was taken. Using this temperature value, a model of the black-body profile can be made. This profile needs to be adjusted from a true black-body emission to account for the emissivity of Tungsten. The spectral emittance of a Tungsten filament is described by the Planck formula:

$$E_{\lambda W}(\lambda, T) = \varepsilon(\lambda, T) \frac{2\pi c^2 h}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} \quad (6)$$

Where $\varepsilon(\lambda, T)$ is the spectral emissivity factor for Tungsten, which is a function of both wavelength and temperature. To simplify matters, over the pertinent visible wavelength (400-700 nm), the value of ε is reasonably constant and can be taken from a number of online tables [19] as being around 0.35 for typical filament bulb. Using the calculated filament temperature and equation 6 the ‘true’ blackbody profile can be modelled and used as the known irradiance of a calibration source $f_{std}(\lambda)$ and used in equation 2 to find the instrument response $R_{de}(\lambda)$.

Because the aim of the tungsten bulb method of calibration is to utilise an approximate blackbody source of known temperature, and hence model its spectral profile, it is possible that the sun could provide a zero cost (all be it intermittent) calibration source. The sphere, spectrometer and a software equipped laptop were taken outside at noon on a bright cloudless day. The open laser pointer port of the integrating sphere was simply pointed at the Sun and a spectrograph of the solar flux taken. This measured spectrum can then be compared with ASTM Terrestrial Reference Spectra: ASTM G-173-03 (AM1.5G) [20]. This is a spectrum of solar irradiance, taking into account factors such as atmospheric absorption, which is significantly different from an ideal black-body at shorter wavelengths. Originally devised for the photovoltaic industry, it provides a good estimate of what the measured spectrum should be. The measured and standard solar spectral profiles require smoothing to remove the distinct absorption peaks; this was done using Excel to fit a spline function through a number of key values. By

taking a smoothed version of AM1.5G as the calibration source of known irradiance $f_{std}(\lambda)$ and the measured solar spectrum as $L_{std}(\lambda)$ using equation 2, the instrument response $R_{de}(\lambda)$ can be interpolated.

2.6. Experimental Samples

Two specific types of reference sample were used in test experiments of the integrating sphere. Anthracene powder was crushed and applied to a quartz disk substrate; this was used as a reference calibration standard, as PLQY values are well established in literature [21]. The second type of sample was spin-coated films of the polyfluorene semiconductor poly[(9,9-dioctylfluorene)-2,7-diyl-alt-(4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole)-2',2''-diyl] (or F8TBT), also on account of the widespread reporting of PLQY in this category of materials, due to their putative applications in optoelectronics [22]. For general demonstration purposes, fluorescent card or plain paper marked with highlighter pen ink was used, being cut and glued to ordinary metric M5 metal washers, thus providing a simple, cheap and durable sample set.

2.7. PLQY Calculations

The method of deMello et al [9] requires three experimental configurations as shown in figure 3.

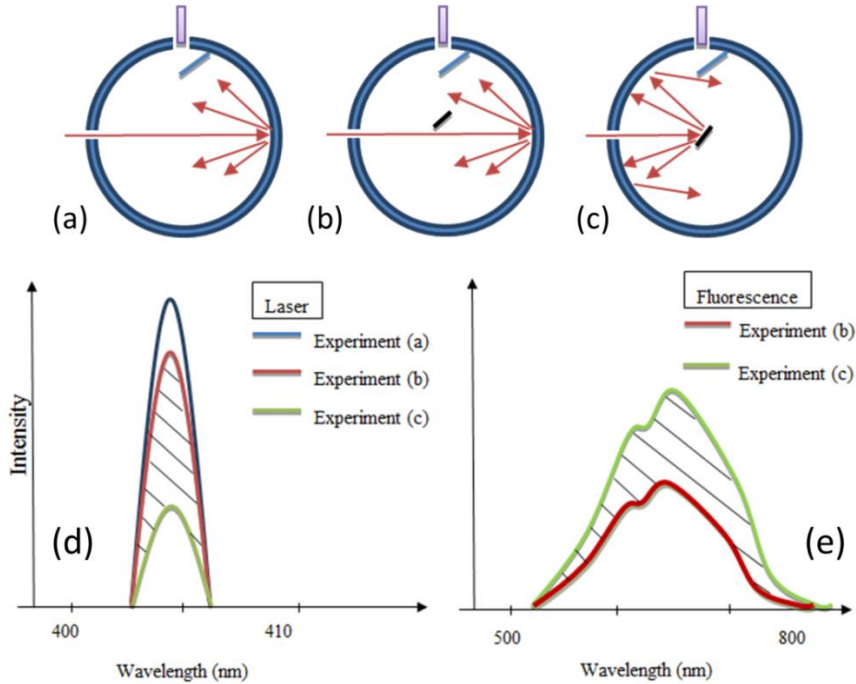


Figure 3. The three experimental configurations used for quantum efficiency measurements are illustrated. In (a), the sample is absent from the sphere, in (b) the laser beam is “missing” the sample, and in (c) the beam is directly illuminating the sample. The sketch graphs below illustrate the corresponding spectra for each configuration, as indicated, showing the laser spectrum in (d) and the fluorescence/photoluminescence spectrum in (e).

In each of the experiments, the area between the curves shown hatched in figures 3d and 3e is proportional to the amount of absorbed laser light. In set-up (c), a fraction A of the incident laser light is absorbed by the sample, the remaining fraction $(1-A)$ will be scattered to the walls of the sphere. A further fraction of this scattered light (μ) will be reabsorbed by the whole surface of the sample. Taking L_a , L_b and L_c to be the areas under the laser illumination profile for each experiment respectively, equations 7 and 8 can be derived.

$$L_b = L_a(1 - \mu) \quad (7)$$

$$L_c = L_a(1 - A)(1 - \mu) \quad (8)$$

From these, an expression for the absorption coefficient A can be obtained:

$$A = \left(1 - \frac{L_c}{L_b}\right) \quad (9)$$

Taking the area under the fluorescence spectra to be E_b (emission from indirect illumination) and E_c (emission from direct illumination), it can be determined that the total light incident on the detector is composed of both unabsorbed laser light and emission from the sample. In set-up (b) this detected light is composed of $L_b + E_b$. In set-up (c), a fraction A of the laser light is absorbed leaving $(1-A)$ reflected, the contribution of the scattered light to the detected total can then be defined as:

$$(1 - A)(L_b + E_b) \quad (10)$$

The emission from the sample due to the excitation of the laser light is:

$$\Phi L_a A$$

Where Φ is the PLQY. This also contributes to the total measured spectrum, so with consideration of all the contributing factors, the total intensity measured over the whole spectrum is given by equation 12.

$$L_c + E_c = (1 - A)(L_b + E_b) + \Phi L_a A \quad (12)$$

This can then be rearranged for quantum yield substituting equation 9

$$\Phi = \frac{E_c - (1-A)*E_b}{L_a A} \quad (13)$$

A sample Scilab script is provided in *supplementary information*, which takes a CSV file input of each spectra, uses a calibration file to adjust the intensity of the data and calculates the areas under each curve. It then calculates PLQY using equation 13.

2.8. Errors

The method of calculating error propagation through the system is similar to that proposed by Johnson et al [23]. Using equation 13 and following the principal of propagating uncertainty [24], the relative uncertainty for the PLQY can be defined as:

$$\frac{U\phi}{\phi} = \sqrt{5(dL)^2 + 2(dE)^2} \quad (14)$$

Where dL is the estimated percentage error on the area of laser intensity and dE is the estimated percentage error on the area of fluorescent emission.

The uncertainties arise from 4 main sources; calibration error, detection system, excitation laser and the sample. An example error budget is shown in Table 1.

Table 1. Error budget for influencing factors NIST calibration.

Element	Uncertainty (%)
Calibration Error (NIST)	
<i>Alignment & Distance</i>	2.00*
<i>Power supply stability</i>	0.50
<i>Field stability</i>	0.31
<i>Spatial Uniformity</i>	0.01
<i>Sphere Input Aperture</i>	2.50
Total	3.26
Spectroscopic Error	
<i>Temperature variance</i>	0.10*
<i>Spectroscope stability</i>	0.50
<i>Sphere reflectance uniformity</i>	1.00*
<i>Light Leak</i>	0.10
Total	1.13
405nm Laser pen stability	5.00*
Sample Self-absorption	1.00*

*Items marked * have no direct specification and are estimated from equivalent literature searches.*

Table 2. The result of calibration method on percentage error dL (area of laser intensity) and dE (area of fluorescent emission). Total error is propagated from equation 14.

Method	dL (%)	dE (%)	Total Error (%)
Solar	7.4	5.4	18.3
Tungsten Bulb	7.2	5.2	17.7
NIST	6.1	3.5	14.5

Combined uncertainties produce values for dL and dE depending on the calibration source. The values from Table 2 and equation 14 are incorporated into the Scilab code used to evaluate the spectral data, producing a direct error value on the PLQY calculation.

3. Results and Discussion

3.1. Reflectance coating and calibration

Shown in Figure 4(a) is the spectral response of both commercially available and the homemade reflectance coating materials. The commercial Avian-B product ranges over 90-95% in this preparation. The DIY coating of a 99% purity Barium Sulphate powder mixed with 1% (by weight) PVA has a very similar range at 90-94% however as can be seen the response is reversed in the wavelength range under

consideration. In terms of cost, Avian-B is currently £200 per 250ml. To manufacture an equivalent quantity of the DIY coating would cost approximately £5 in materials.

The response curves for the two different calibration methods are shown in figure 4(b) and also a NIST verified spectral irradiance lamp. Using anthracene as a test standard the three different methods of calibration produced a variation in results, the NIST lamp route being closest to literature but such a lamp costs around \$9000 US. The Tungsten bulb method of calibration is very close to that of a NIST certified light source and within the 15% estimated by Kosche and Harang [18]. The cost of the bulb and holder should be under £5. The solar method is the least accurate, but still resulted in values within 15-20% at notionally zero cost.

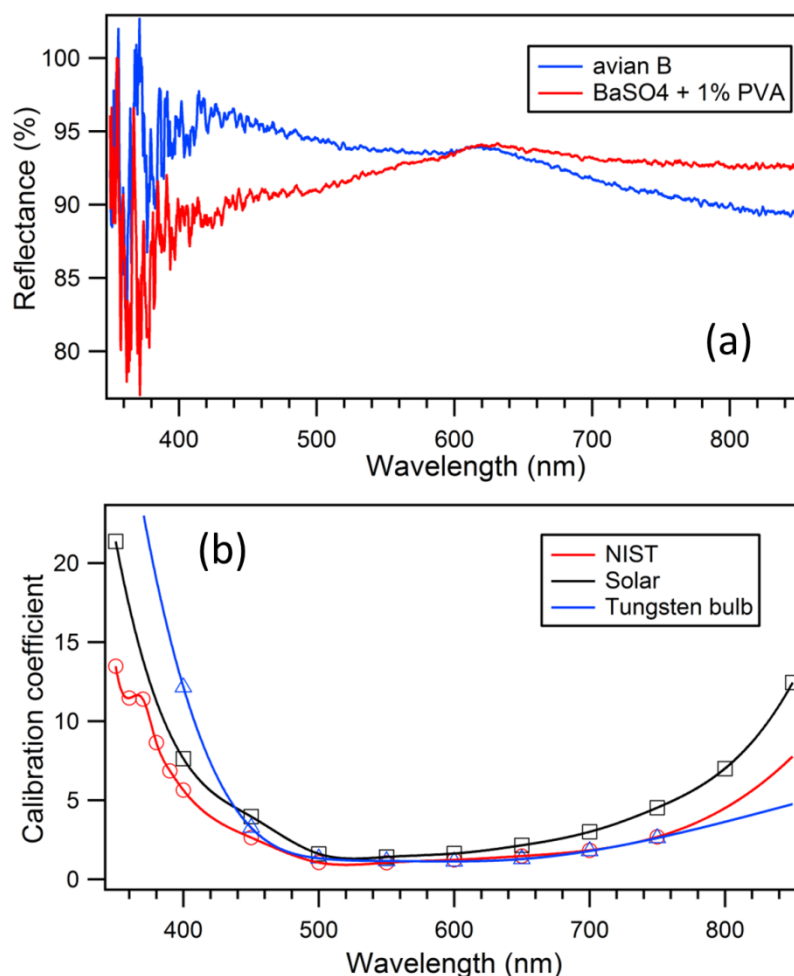


Figure 4. (a) Broadband reflectance spectra for commercial (avian B) and homemade (BaSO_4) coating materials, (b) instrumental response functions as derived for different calibration methods, as indicated.

3.2. PLQY of samples

Figure 5(b) shows the result of placing a sample of ground Anthracene powder into the sphere and processing it through the SciLab code using the Tungsten bulb (at 2350 K) calibration method. The sample craft card used unknown ink and pigment, however the PLQY (Figure 5(a)) results shows the relative fluorescent efficiency was easily determined. All the test measurements carried out are summarised in Tables 3 and 4; in all cases the PLQY values derived showed a very good agreement with literature, to within a fractional level of a few %, with the exception of Pyranine where literature states its PLQY as a 'pure' substance in solution not as a commercial 'highlighter pen' product.

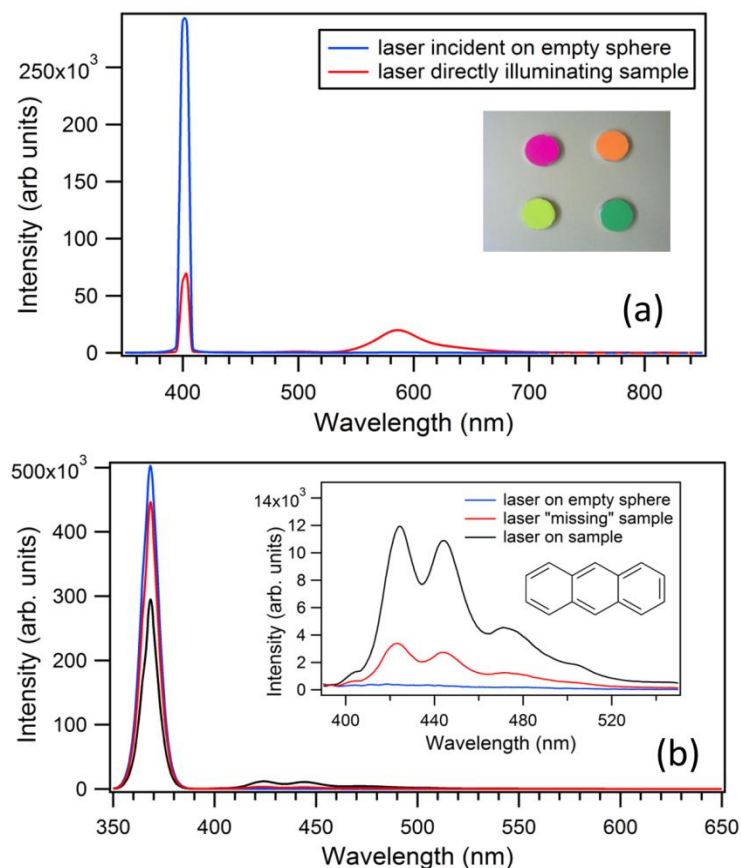


Figure 5. (a) Example data of PLQY measurement, as obtained for the fluorescent card sample 1, using the tungsten bulb calibration; PLQY was measured as 0.51 ± 0.09 . The inset shows samples of fluorescent card mounted on metal washers, (b) shows the spectra for PLQY measurement for a sample of ground anthracene powder, also using the tungsten bulb calibration method; PLQY was measured as 0.27 ± 0.027 . The inset shows the chemical structure of anthracene.

Table 3. Test Sample PLQY variation with different calibration methods.

Sample	Calibration Method			
	Solar	Tungsten Bulb	NIST	Literature[21-23]
Anthracene @ 365 nm	0.18 ± 0.029	0.24 ± 0.027	0.22 ± 0.025	0.27 [21]
F8TBT @ 405 nm	0.09 ± 0.016	0.12 ± 0.021	0.10 ± 0.014	0.11 [22]
Pyranine (highlighter pen) @ 405 nm	0.65 ± 0.118	0.69 ± 0.122	0.65 ± 0.094	0.90 [23]

Table 4. PLQY of Fluorescent Card samples using 405 nm laser pointer

Sample	Calibration Method		
	Solar	Tungsten Bulb	NIST
Fluorescent Card 1 @ 405 nm	0.49 ± 0.089	0.51 ± 0.090	0.52 ± 0.075
Fluorescent Card 2 @ 405 nm	0.23 ± 0.042	0.26 ± 0.046	0.25 ± 0.036
Fluorescent Card 3 @ 405 nm	0.27 ± 0.049	0.29 ± 0.051	0.27 ± 0.039
Fluorescent Card 4 @ 405 nm	0.47 ± 0.086	0.50 ± 0.089	0.48 ± 0.069

4. Conclusions

The aim of the project was to design and manufacture an experimentally accurate instrument that is able to easily and reliably establish the absolute photo-luminescent quantum yield of some fluorescent materials presented as solid films. The project makes novel use of 3D printing to manufacture an integrating sphere, thereby allowing a custom design which can accommodate sample specific features. It does this at a cost low enough for most schools and undergraduate laboratories, assuming access to a spectrometer, 3D printer and general workshop facilities are available.

Following the experimental procedure of deMello *et al* [9] provides results that suitably account for re-absorption and re-emission of the illuminated sample. Calibration to establish absolute values is conducted as proposed by Johnson *et al* [23] with reference to a certified blackbody illumination standard. The confirmation of calibration by the use of a well-documented fluorescence standard (anthracene) means that results for the samples on test have a high degree of confidence. The sensitivity of the equipment was sufficient to detect photo-bleaching [26] of the samples during data gathering. A further final year student project to fully characterise these effects in organic semiconductor materials is in progress, thus potentially addressing pertinent research questions in that field.

This novel approach provides a low cost means of manufacture, which prompted investigations of other low cost features such as homemade DIY reflectance coatings, the results of which showed some merit particularly considering the cost to performance ratio. The use of a laser pointer as a low cost excitation light source and the evaluation of a simple method of calibration using a standard tungsten bulb, or even the Sun, makes this kind of experiment available to most undergraduate labs as a teaching tool to reinforce concepts learnt in modules such as optics, optronics, and semiconductor physics, whilst still maintaining an acceptable degree of experimental accuracy for useful quantitative science.

This paper illustrates the use of certain technological innovations (such as 3D printing) in the planning and delivery of undergraduate physics student projects; providing low-cost instrumentation solutions, which would otherwise be inaccessible to such undergraduate level projects. This project also leaves a clear legacy, in terms of new apparatus enhancing the scope of future projects, and for potential use in prescient research in the area of photoluminescent materials.

Acknowledgments

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References

- [1] Exley K. *Key aspects of teaching and learning in science and engineering*. Fry H, editor. London: Kogan Page; 1999.
- [2] <http://www.aber.ac.uk/en/phys/prospective/>
- [3] Stokes GG. 1852 On the change of refrangibility of light. *Phil. Trans. R. Soc. Lon.* **142** 463-562.
- [4] Stepanenko O, Verkhusha V, Kuznetsova I, Uversky V, Turoverov K. 2008 Fluorescent proteins as biomarkers and biosensors: Throwing color lights on molecular and cellular processes. *Curr. Protein Pept. Sc.* **9(4)** 338-69.
- [5] Burroughes J, Bradley D, Brown A, Marks R, Mackay K, Friend R, Burn P, Holmes A. 1990 Light-Emitting-Diodes Based On Conjugated Polymers. *Nature.* **347(6293)** 539-541.

- [6] Finlayson CE, Amezcua A, Sazio PJA, Walker PS, Grossel MC, Curry RJ, Smith D, Baumberg J. 2005 Infrared emitting PbSe nanocrystals for telecommunications window applications. *J. Mod. Optic.* **52(7)** 955-64.
- [7] Shuai Z, Beljonne D, Silbey R, Bredas J. 2000 Singlet and triplet exciton formation rates in conjugated polymer light-emitting diodes. *Phys. Rev. Lett.* **84(1)** 131-4.
- [8] Greenham N, Samuel I, Hayes G, Phillips R, Kessener Y, Moratti S, Holmes A, Friend R. 1995 Measurement Of Absolute Photoluminescence Quantum Efficiencies In Conjugated Polymers. *Chem. Phys. Lett.* **241(1-2)** 89-96.
- [9] deMello J, Wittmann H, Friend R. 1997 An improved experimental determination of external photoluminescence quantum efficiency. *Adv. Mater.* **9(3)** 230-232.
- [10] Crosby G, Demas J, Callis J. 1972 Absolute Quantum Efficiencies. *J. RES.NBS. C. ENG. INST. A* **76(6)** 561-577.
- [11] Labsphere Technical Guide *Reflectance Materials and Coatings*.
<https://www.labsphere.com/technical-library/>
- [12] Leyre S, *et al.* 2014 Absolute determination of photoluminescence quantum efficiency using an integrating sphere setup. *Rev. Sci. Instrum.* **85** 123115.
- [13] <http://www.rs-online.com/designspark/electronics/eng/page/mechanical>
- [14] <http://www.conrad-electronic.co.uk/ce/en/product/1395717/3D-printer-Renkforce-Dual-extruder>
- [15] <https://www.gov.uk/government/publications/laser-radiation-safety-advice/laser-radiation-safety-advice>
- [16] <http://oceanoptics.com/product/ws-1-reflectance-standards/>
- [17] Labsphere Technical Guide *Integrating Sphere Theory and Applications*.
<https://www.labsphere.com/technical-library/>
- [18] Kosch M, Mäkinen S, Sigernes F, Harang O, Lorentzen D. Absolute optical calibration using a simple tungsten light bulb: Experiment. *Proceedings of the 30th Annual European Meeting on Atmospheric Studies by Optical Methods*. 2003.
- [19] Table of Total Emissivity: www.omega.co.uk/temperature/z/pdf/z088-089.pdf.
- [20] Nayak P K, Garcia-Belmonte G, Kahn A, Bisquert J, Cahen D. 2012 Photovoltaic efficiency limits and material disorder *Energy Environ. Sci.* **5** 6022
- [21] Suzuki K. Quantaurus-QY 2011 Absolute photoluminescence quantum yield spectrometer. *Nat. Photonics*, **5(5)** 247-314
- [22] Lu L, Finlayson C E, Kabra D, Albert-Seifried S, Song M, Havenith R, Tu G, Huck W, Friend R. 2013 The Influence of Side-Chain Position on the Optoelectronic Properties of a Red-Emitting Conjugated Polymer. *Macromol. Chem. Phys.* **214(9)** 967-974.
- [23] Johnson A R, Lee S, Klein J. 2007 Absolute photoluminescence quantum efficiency measurement of light-emitting thin films *Rev. Sci. Instrum.* **78** 096101.
- [24] International Organization for Standards (ISO): Guide to Expression of Errors in Measurements 1995 & JCGM 104:2009
- [25] Legenzov E, Dirda N, Hagen B, Kao J. 2015 Synthesis and Characterization of 8-O-Carboxymethylpyranine (CM-Pyranine) as a Bright, Violet-Emitting, Fluid-Phase Fluorescent Marker in Cell Biology. *PLOS ONE*. **10(7)** e0133518.
- [26] Dittrich P, Schwille P. 2001 Photobleaching and stabilization of fluorophores used for single-molecule analysis with one- and two-photon excitation. *Appl. Phys. B-Lasers O.* **73(8)** 829-837.

Supplementary Information

- CAD models and stereo lithography (STL) files for 3D printing.
- Scilab script for PLQY calculation
- Figures File