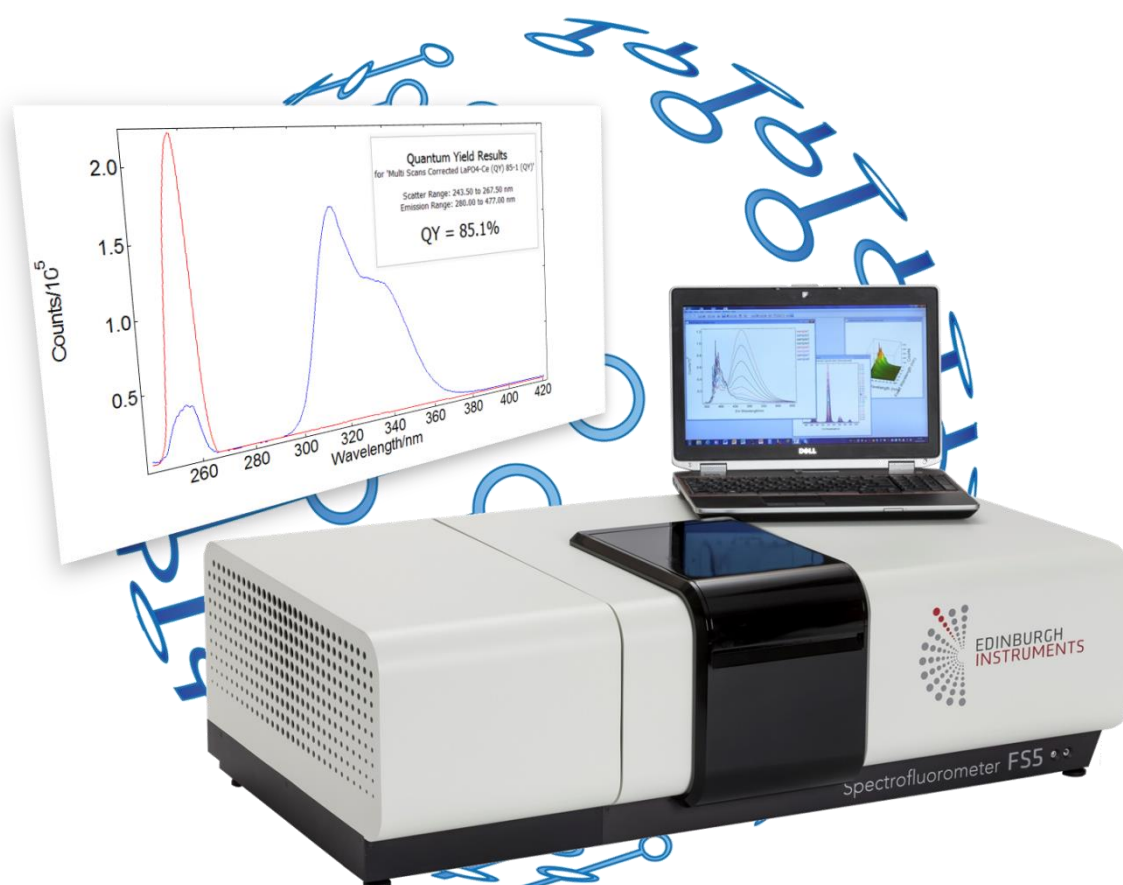


Absolute quantum yield of UV- to NIR-emitting samples

Georgios Arnaoutakis

AN_P19 v.1

DATE 15 Sep. 15



Edinburgh Instruments Ltd
2 Bain Square,
Kirkton Campus,
Livingston, United Kingdom
EH54 7DQ

AN_P19

Copyright © 2015. Edinburgh Instruments Ltd. All rights reserved

Telephone (UK)
+44 (0)1506 425 300
Telephone (North America)
1-800-323-6115

Email
enquiries@edinst.com
Website
www.edinst.com

Introduction

The photoluminescence quantum yield (QY) or quantum efficiency η is one of the core parameters in the characterisation of luminescent materials^{1,2}. The absolute QY, defined as the ratio of the photons emitted by the material over the absorbed photons, has widely replaced the relative QY method, requiring a fluorescent standard of known QY. It also constitutes a simpler method relying on minimum alignment and calibration compared to thermal lens/beam deflection and photoacoustic methods³. Instead, a fluorescence spectrometer equipped with an integrating sphere is employed in the absolute method.

Methods & Materials

Liquid and solid materials were measured spanning excitation and emission wavelengths from the UV to the NIR. LED phosphor powders and thin films doped with lanthanides such as Cerium (Ce^{3+}), Terbium (Tb^{3+}) and Europium (Eu^{2+}) were measured in standard PTFE trays. In the NIR range, semiconductor nanocrystal lead sulfide (PbS) quantum dots (QD-NIR-1V, Ocean Optics) in toluene were dispensed into 10 mm path-length quartz cuvettes.

Excitation and emission spectra were measured in a fluorescence spectrometer FS5-NIR equipped with an integrating sphere module (SC-30) and a single photon PMT detector (Hamamatsu, R2658P) extending the emission detection range to 1010nm. For liquid samples a measurement over the scattering L_{sam} and emission E_{sam} of the sample, followed by a measurement of the solvent, also called reference or blank, L_{ref} and E_{ref} , as:

$$QY = E_{\text{sam}} - E_{\text{ref}} / L_{\text{ref}} - L_{\text{sam}}$$

For solid powder and thin film samples three measurements were performed for the calculation of the quantum yield: i) A measurement of the scattering without the sample, L_{ref} , ii) a measurement of the emission of the sample under direct excitation, E_{samdir} , and iii) a measurement of the scattering with the sample under indirect excitation, E_{samind} , as⁴:

$$QY = E_{\text{samdir}} - [1 - (1 - L_{\text{samdir}}/L_{\text{samind}})] E_{\text{samind}} / L_{\text{ref}} (1 - L_{\text{samdir}}/L_{\text{samind}})$$

The calculation of the QY was performed in the wizard of the instrument's operating software, Fluoracle.

Results – Discussion

Figures 1 and 2 display the scattering and emission spectra of Ce^{3+} and $\text{Ce}^{3+}/\text{Tb}^{3+}$ -doped phosphor, respectively.

In addition to the intense green emission, the QY increases from 85.1% for the Ce^{3+} -doped phosphor to 92% for $\text{Ce}^{3+}/\text{Tb}^{3+}$ -doped phosphor^{5,6}.

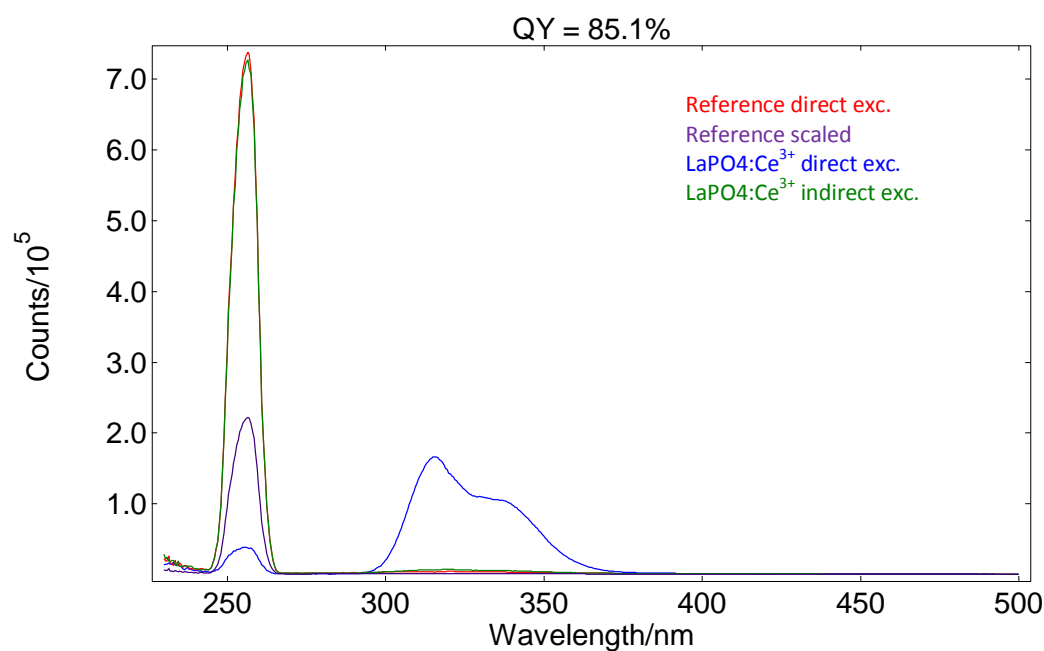


Figure 1: Scattering and emission spectra of $\text{LaPO}_4:\text{Ce}^{3+}$ phosphor. The measurement conditions were: $\Delta\lambda_{\text{exc}}=10\text{nm}$, $\Delta\lambda_{\text{em}}=1\text{nm}$, step=0.5nm, dwell=0.2s.

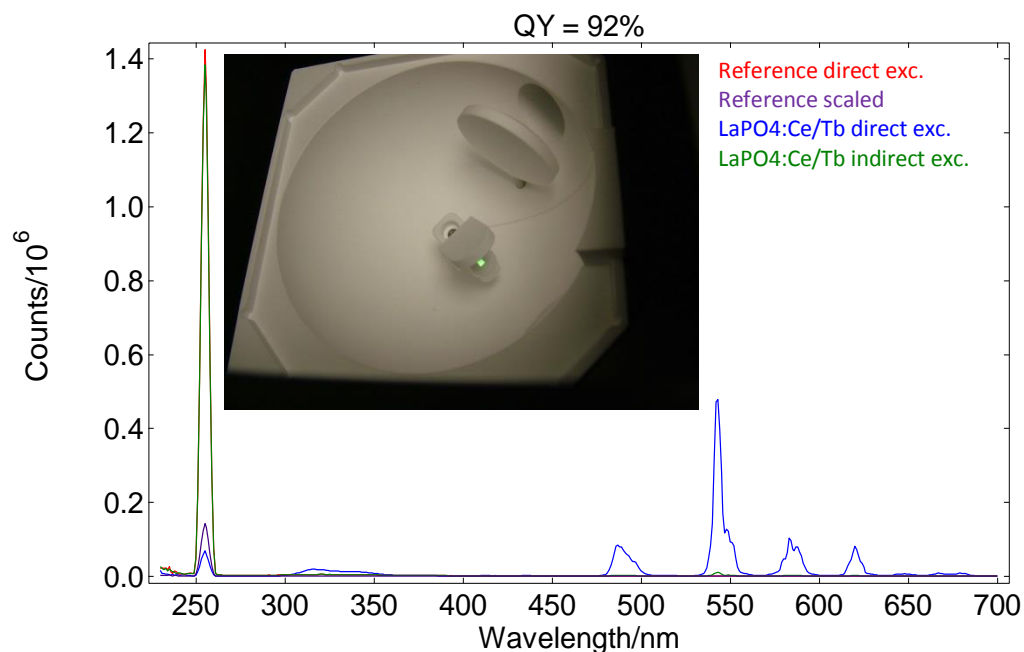


Figure 2: Scattering and emission spectra of $\text{Ce}^{3+}/\text{Tb}^{3+}$ -doped phosphor. The measurement conditions were: $\Delta\lambda_{\text{exc}}=10\text{nm}$, $\Delta\lambda_{\text{em}}=0.5\text{nm}$, step=0.25nm, dwell=0.1s.

Scattering, direct and indirect excitation emission spectra of a Eu^{2+} -doped thin film and PbS quantum dots can be seen in Figure 3 and 4, respectively. Note the considerable emission measured under indirect excitation of the thin film in the integrating sphere.

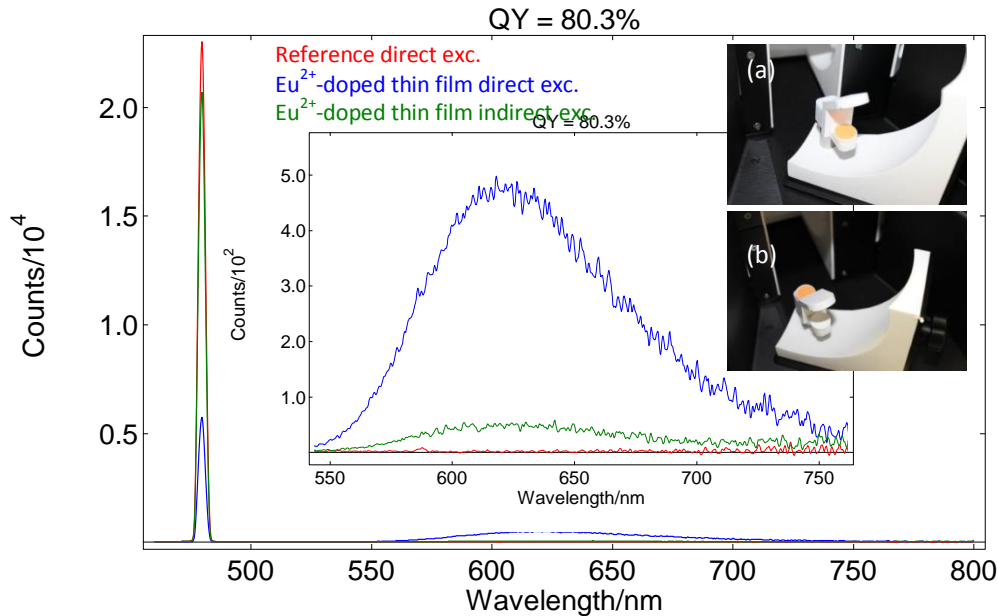


Figure 3: Eu^{2+} -doped thin film under (a) direct and (b) indirect excitation. The samples were excited at 480nm with excitation and emission bandwidths $\Delta\lambda_{\text{exc}}=3\text{nm}$ and $\Delta\lambda_{\text{em}}=0.2\text{nm}$, respectively, with a step of 0.25nm and integration time of 0.1s.

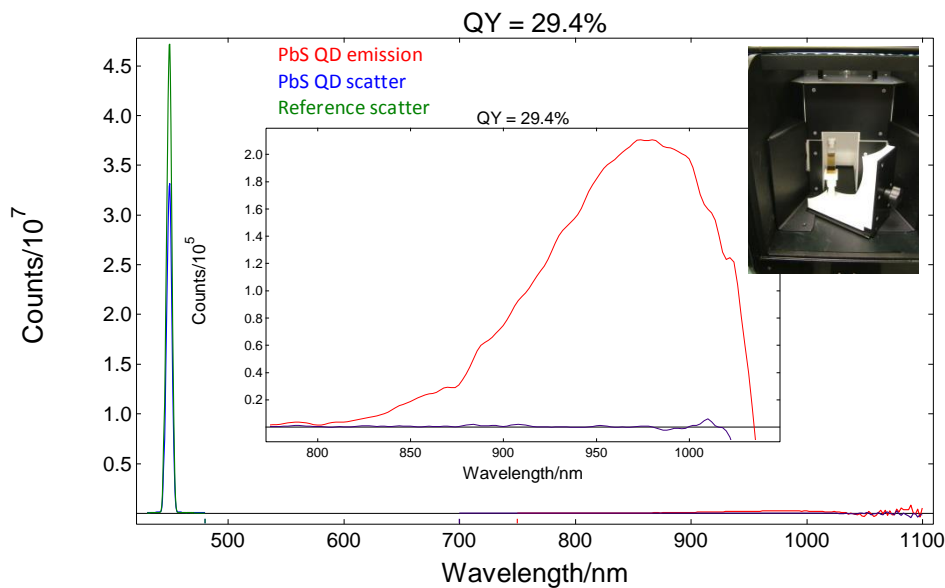


Figure 4: Scattering and emission spectra of PbS quantum dots. Conditions were: $\Delta\lambda_{\text{exc}}=5\text{nm}$, $\Delta\lambda_{\text{em}}=2\text{nm}$, step=1nm, dwell=0.5s.

References

1. Crosby, Glenn A., and James N. Demas. "Measurement of photoluminescence quantum yields. Review." *The Journal of Physical Chemistry* **75.8** (1971): 991-1024.
2. Würth, C., Grabolle, M., Pauli, J., Spieles, M. & Resch-Genger, U. Comparison of Methods and Achievable Uncertainties for the Relative and Absolute Measurement of Photoluminescence Quantum Yields. *Anal. Chem.* **83**, 3431–3439 (2011).
3. Würth, C., Geißler, D., Behnke, T., Kaiser, M. & Resch-Genger, U. Critical review of the determination of photoluminescence quantum yields of luminescent reporters. *Anal Bioanal Chem* **407**, 59–78 (2014).
4. de Mello, J. C., Wittmann, H. F. & Friend, R. H. An improved experimental determination of external photoluminescence quantum efficiency. *Adv. Mater.* **9**, 230–232 (1997).
5. Jüstel, T., Krupa, J.-C. & Wiechert, D. U. VUV spectroscopy of luminescent materials for plasma display panels and Xe discharge lamps. *Journal of Luminescence* **93**, 179–189 (2001).
6. Bühler, G. & Feldmann, C. Microwave-Assisted Synthesis of Luminescent LaPO₄:Ce,Tb Nanocrystals in Ionic Liquids. *Angewandte Chemie International Edition* **45**, 4864–4867 (2006).

Proprietary notice

Words and logos marked with ® or ™ are registered trademarks or trademarks owned by EDINBURGH INSTRUMENTS Limited. Other brands and names mentioned herein may be the trademarks of their respective owners.

Neither the whole nor any part of the information contained in, or the product described in, this document may be adapted or reproduced in any material form except with the prior written permission of the copyright holder.

The product described in this document is subject to continuous developments and improvements. All particulars of the product and its use contained in this document are given by EDINBURGH INSTRUMENTS in good faith. However, all warranties implied or expressed, including but not limited to implied warranties of merchantability, or fitness for purpose, are excluded.

This document is intended only to assist the reader in the use of the product. EDINBURGH INSTRUMENTS Limited shall not be liable for any loss or damage arising from the use of any information in this document, or any error or omission in such information, or any incorrect use of the product.

Confidentiality status

This document is Open Access. This document has no restriction on distribution.

Feedback on this Application Note

If you have any comments on this Application Note, please send email to sales@edinst.com giving:

the document title

the document number

the page number(s) to which your comments refer

an explanation of your comments.

General suggestions for additions and improvements are also welcome.