Characterisation of fluorescent materials

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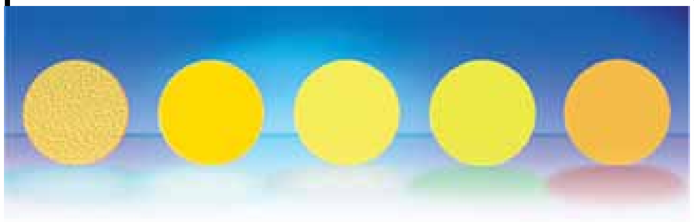
CORM 2011

Introduction

- Characterisation of fluorescent materials:
  - Fluorescent material (phosphor powder)

    - Excitation & emission wavelengths
    - Quantum Efficiency (QE): $\frac{\#\text{ emitted photons}}{\#\text{ absorbed photons}}$
  - Incorporated in carrier material (plastics, glass)



    - Full photon budget
    - Spatial distribution of photons
  - Incorporated in a device

    - EQE
    - Total efficiency

Absolute determination of the quantum efficiency of phosphor powders

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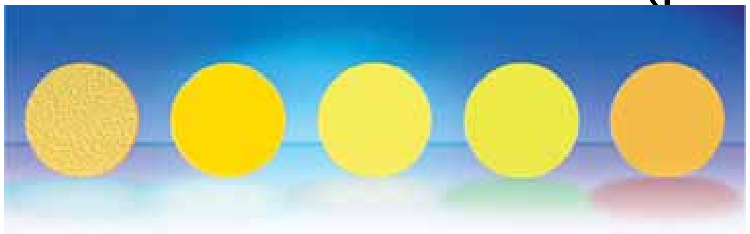
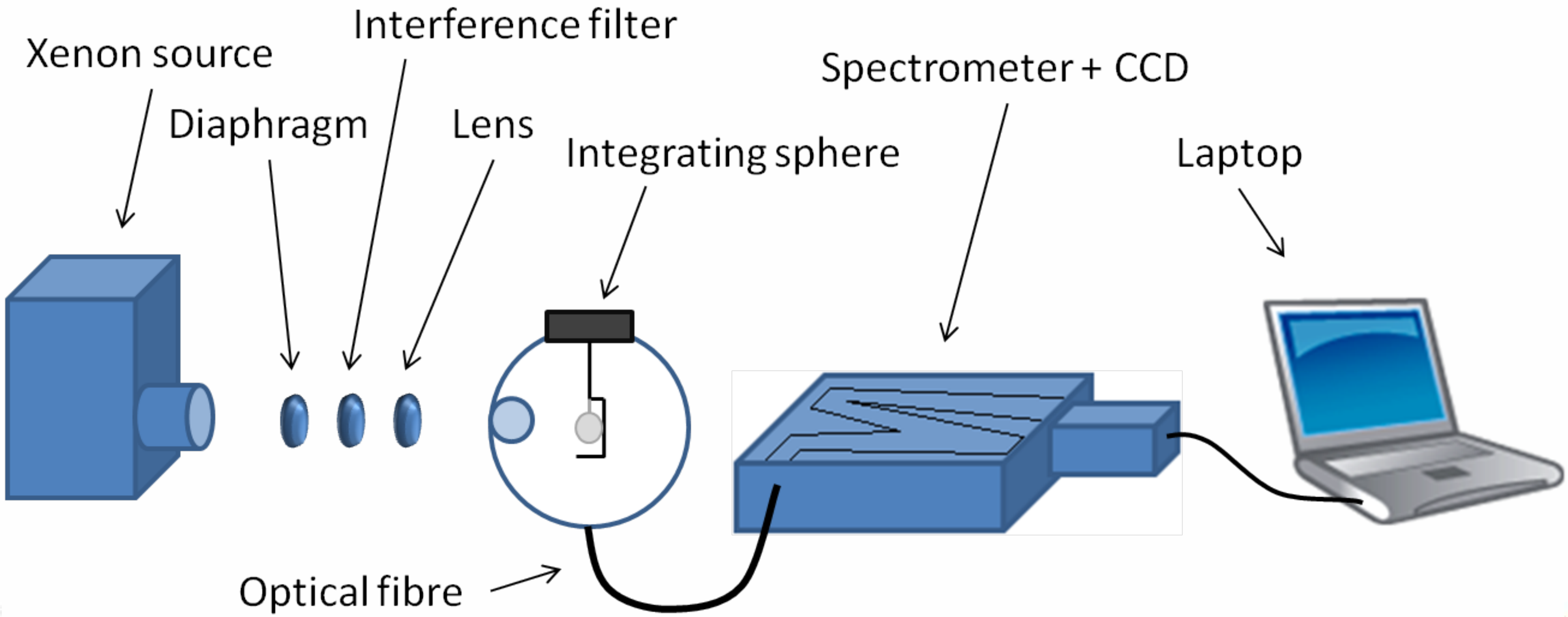


  - Incorporated in a device

Measurement set-up

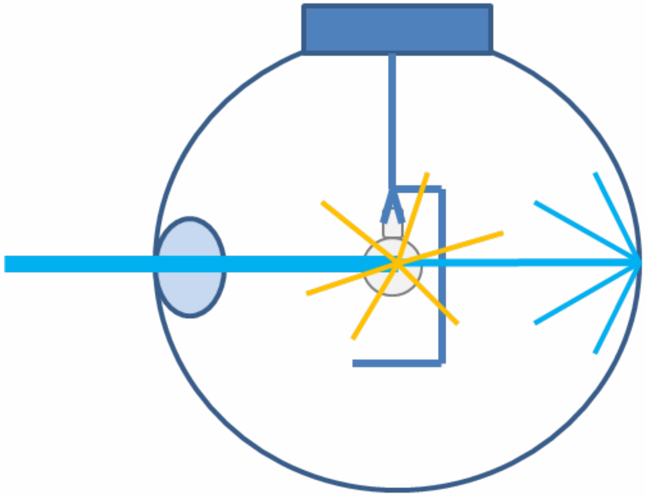
- Our setup: Based on de Mello *et al*.
  - Excitation source
  - Integrating sphere + sample holder
  - Spectrometer + CCD
  - PC



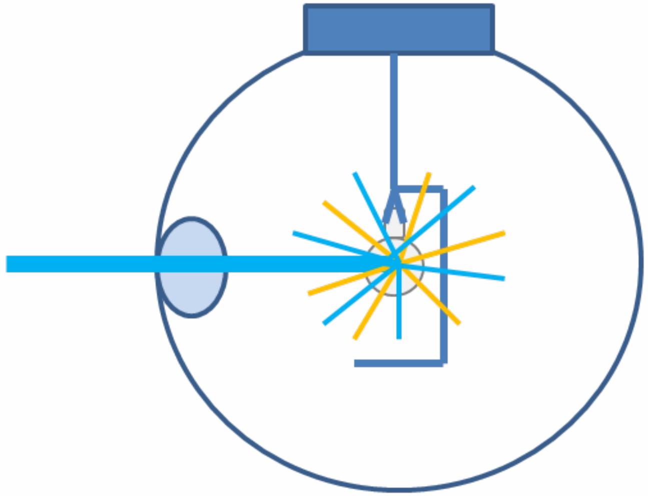
Sample preparation

- Small amount of phosphor in cuvette
  - Small substitution error
  - Reduced self-absorption

- The cuvette has diffuse side walls
  - Similar optical paths for excitation and emission photons



Clear cuvette windows



Diffuse cuvette windows

Calibration of the set-up

- The relative spectral response of the measurement setup needs to be determined

- Step 1: Calibration of the Xenon light source spectrum
  - After diaphragm and lens
  - With calibrated halogen irradiation standard
  - Only relative spectral calibration is needed

- Step 2: Calibration of the setup with Xenon light source
  - Empty cuvette in sphere
  - Identical light paths for calibration and measurements

Measurement procedure

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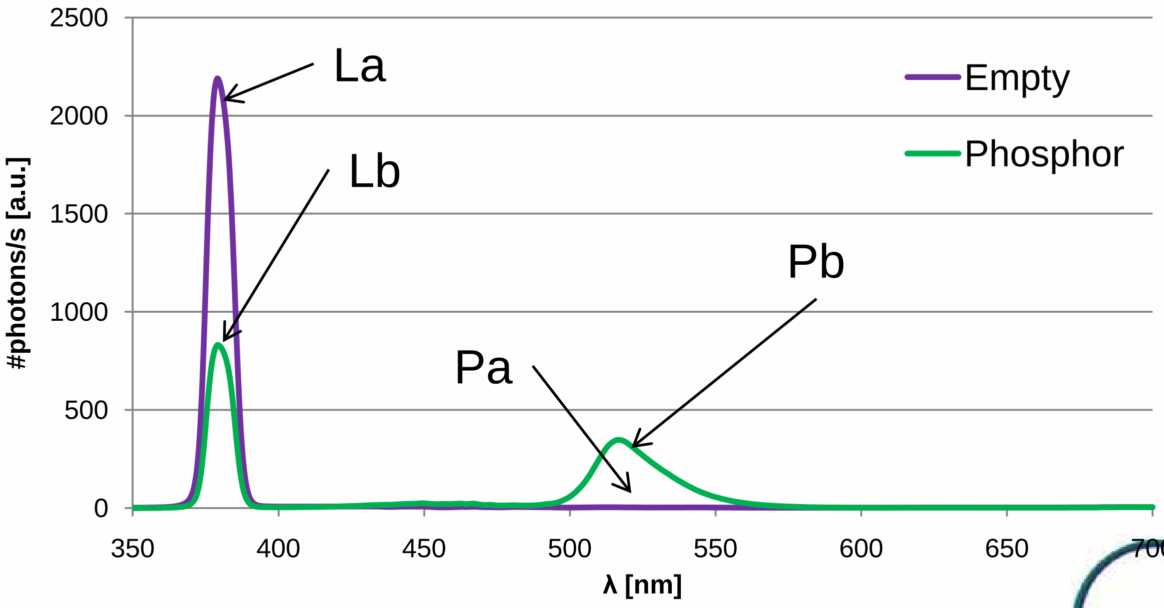
- Step 1: Empty cuvette in sample holder
  - Total number of incident photons/s (“La”)
  - ‘Dark signal’ in the emission wavelength area (“Pa”)
- Step 2: Cuvette with phosphor powder in sample holder
  - Total number of photons/s not absorbed by the phosphor (“Lb”)
  - Total number of photons/s emitted in emission wavelength area (“Pb”)

- $$QE = \frac{\#\text{ emitted photons}}{\#\text{ absorbed photons}}$$

$$= \frac{\text{Pb-Pa}}{\text{La-Lb}}$$



Validation

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- Commercial available phosphor samples:
  - $BaMgAl_{10}O_{19}:Eu^{2+}$ (BAM Blue)
  - $BaAl_{12}O_{19}:Mn^{2+}$ (BAM Green)

- QE at excitation wavelength 380 nm:

Phosphor	Given QE	Measured QE
$BaMgAl_{10}O_{19}:Eu^{2+}$	0.96 ± 0.02	0.96 ± 0.04
$BaAl_{12}O_{19}:Mn^{2+}$	0.83 ± 0.02	0.81 ± 0.04

- Good agreement between given and measured QE.

Problem

- Commercial available phosphor sample:
  - $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce)

- QE at excitation wavelength 460 nm:

Phosphor	Given QE	Measured QE
$Y_3Al_5O_{12}:Ce^{3+}$	0.94 ± 0.02	0.75 ± 0.04

- Large discrepancy between given and measured QE.

Further research

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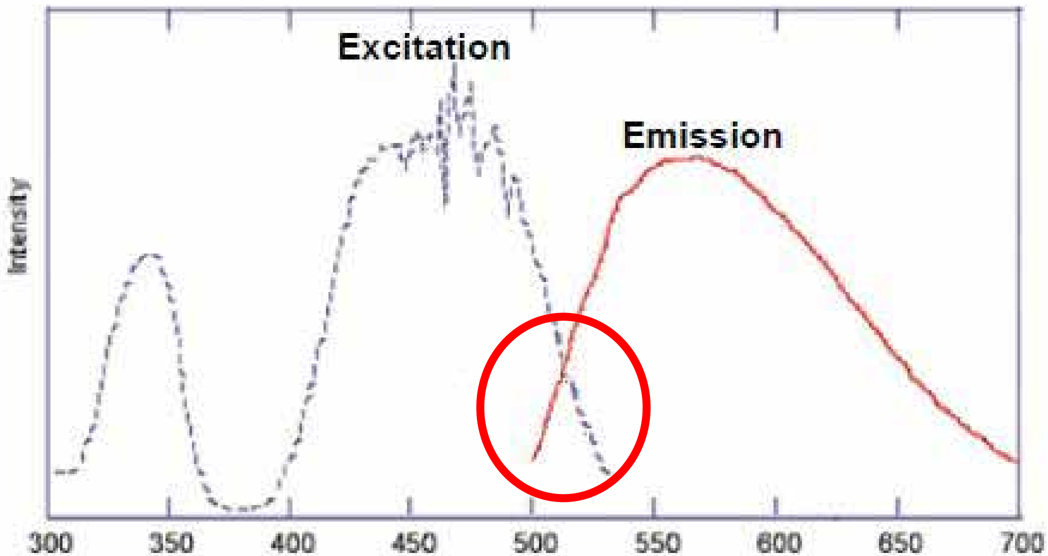
- Large overlap between excitation and emission spectra for YAG:Ce à Possible large amount of self-absorption within the phosphor layer



- Other sample preparation:
  - Incorporate several concentrations of YAG:Ce powder in transparent matrix material (e.g. epoxy)
  - Correlation between concentration and measured QE?

Characterisation of remote phosphor components with spectral BSDF data

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Full Photon Budget

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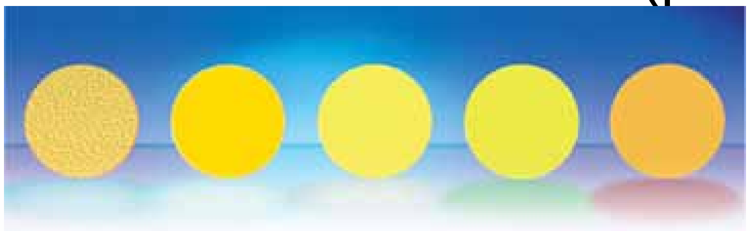
  - Incorporated in carrier material (plastics, glass)



  - Incorporated in a device

Full photon budget

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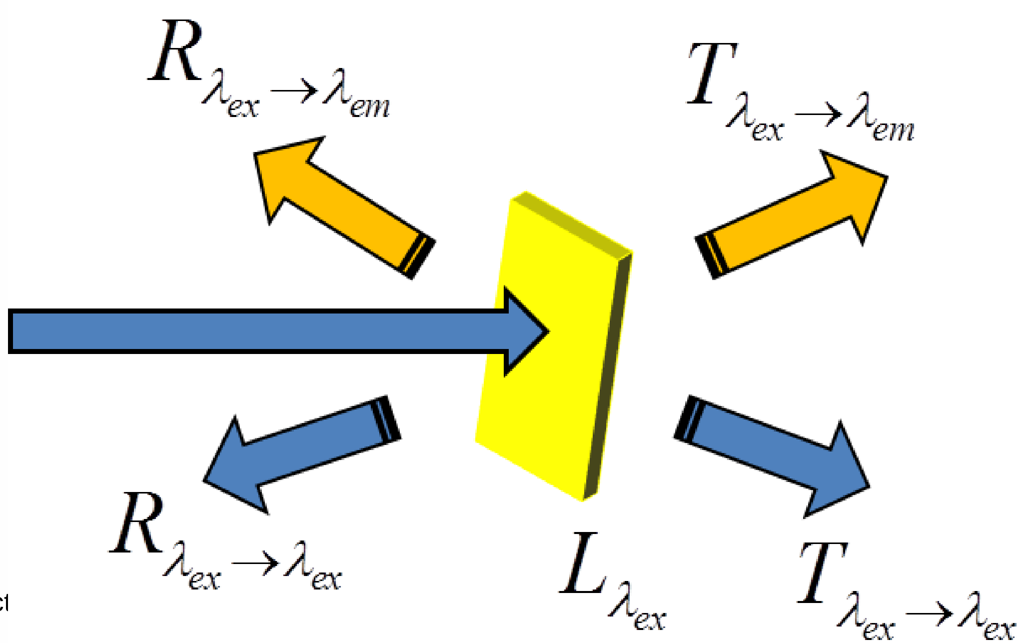
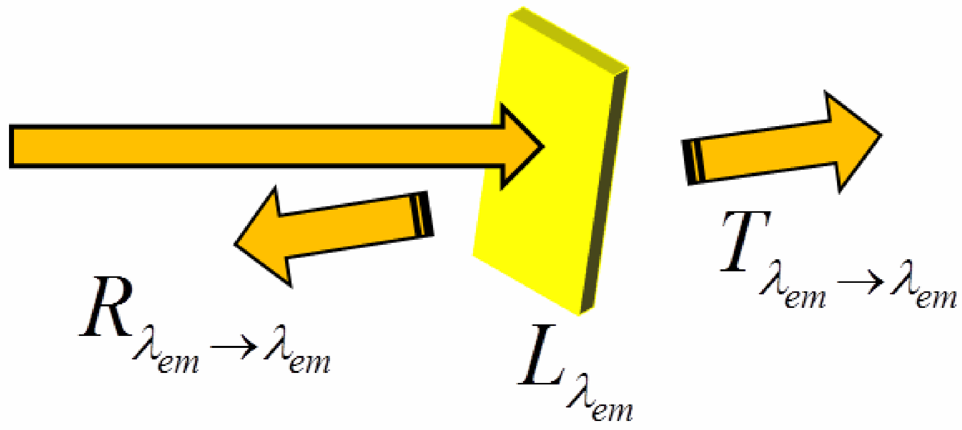
- When incident (excitation) photons hit fluorescent material
  - Pct of photons scattered backwards $R_{\lambda_{ex} \rightarrow \lambda_{ex}}$
  - Pct of photons scattered forward $T_{\lambda_{ex} \rightarrow \lambda_{ex}}$
  - Pct of photons converted and emitted in forward direction $T_{\lambda_{ex} \rightarrow \lambda_{em}}$
  - Pct of photons converted and emitted in backward direction $R_{\lambda_{ex} \rightarrow \lambda_{em}}$
  - Pct of photons lost $L_{\lambda_{ex}}$



Full photon budget

- When incident (emission) photons hit fluorescent material
  - Pct of photons scattered backwards $R_{\lambda_{em} \rightarrow \lambda_{em}}$
  - Pct of photons scattered forward $T_{\lambda_{em} \rightarrow \lambda_{em}}$
  - Pct of photons lost $L_{\lambda_{em}}$



Measurement setup

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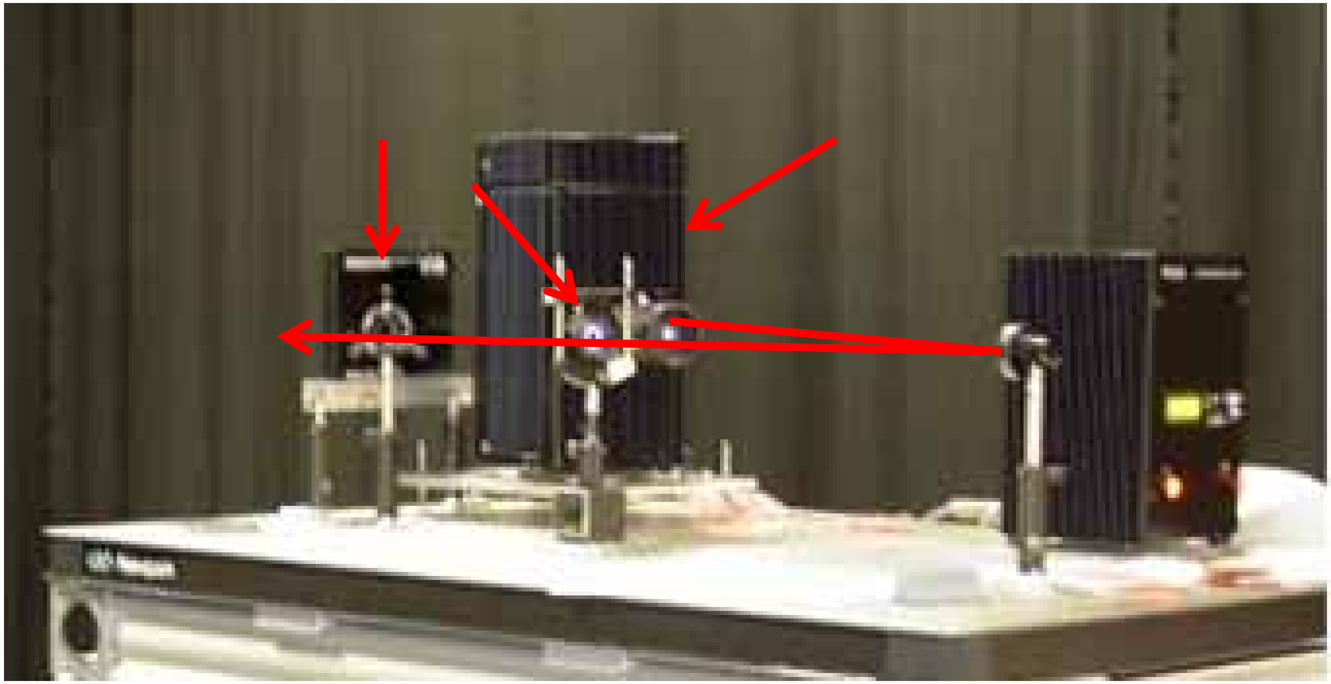
- Spectral BSDF setup – Illumination section:
  - Illumination source: Xenon light source
  - Secondary optics: concave mirror images source onto detector
  - Optical filters can be inserted into the light path for wavelength selection
  - Set of ND-filters in filter wheel can be inserted into the light path



Measurement setup

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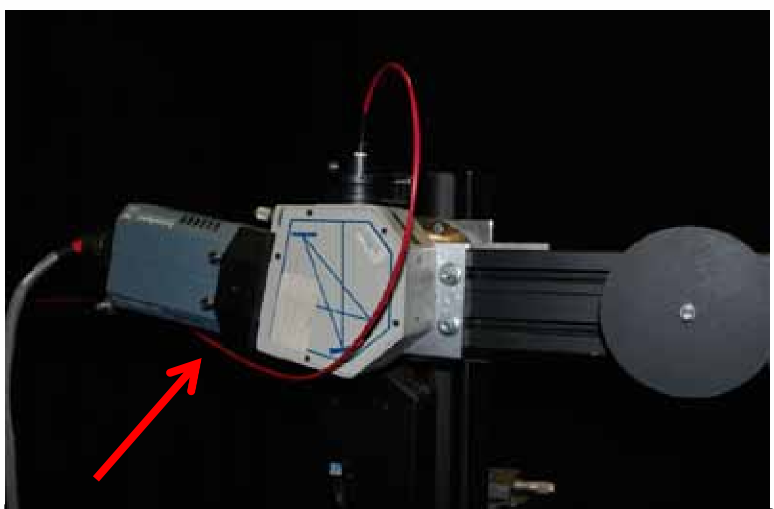
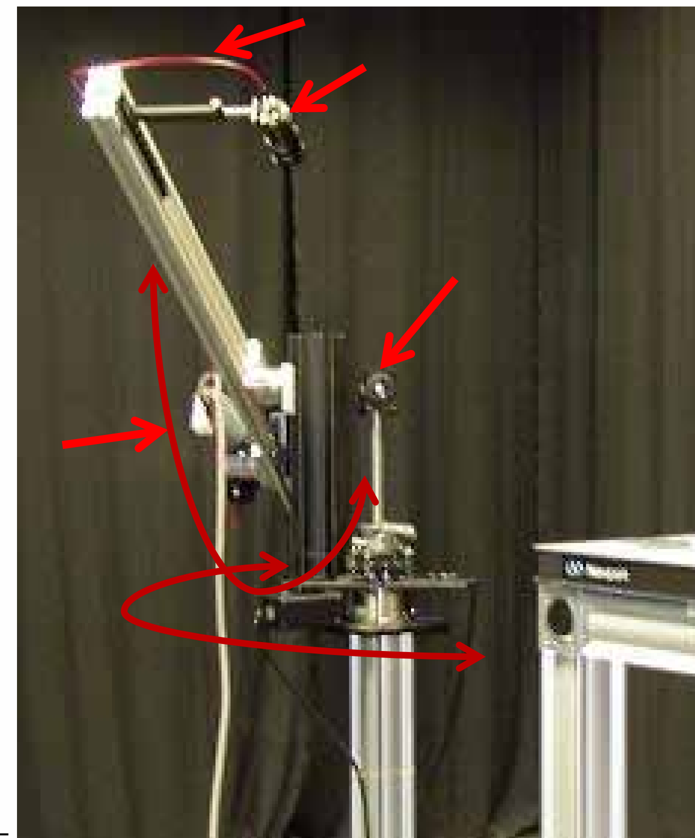
- Spectral BSDF setup – Detection section:
  - Detector head: diaphragm, quartz lens, integrating cylinder and optical quartz fibre
  - The quartz fibre is connected with a spectrograph with Si-CCD
  - Detector head can be positioned with two stepper motors
  - Angle of incidence can be changed by rotating the sample holder.





Calibration of the set-up

- Determination of the relative spectral response is needed
  - 200 – 350 nm: Deuterium calibration source
  - 550 – 800 nm: Halogen calibration source
  - 350 – 550 nm: Halogen calibration source with short wave pass filter

  à To avoid stray light contamination

- Second order distortion is not a problem:
  - Between 200 – 400 nm: SR drops to 0 below 200 nm
  - Above 400 nm: Halogen source has very little output below 400 nm + the SR is much lower

Measurement procedure

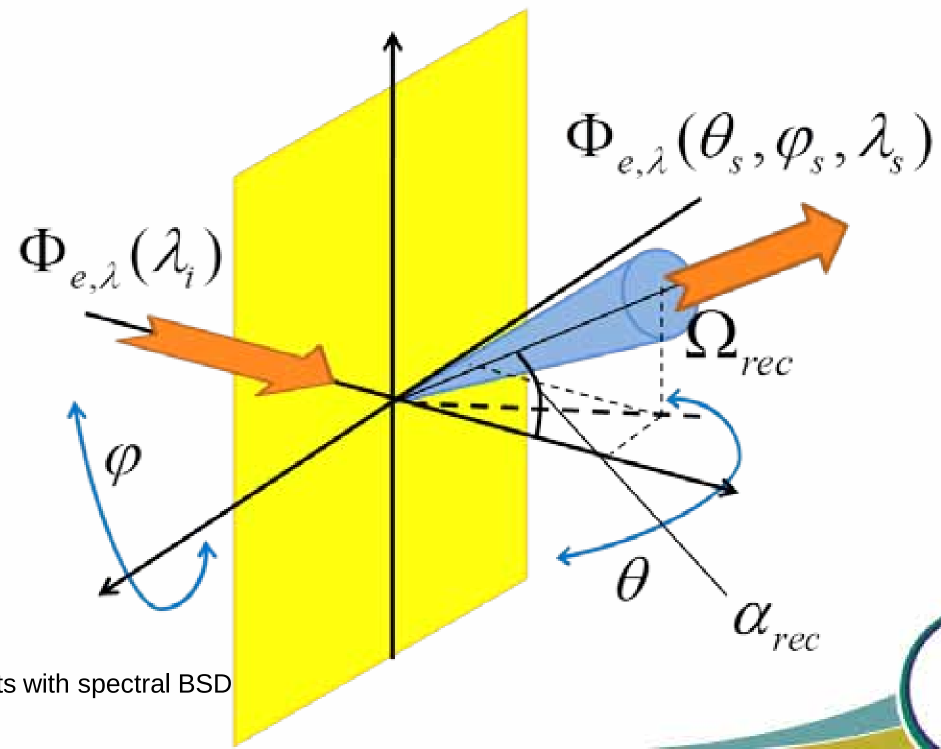
- Calculation of the spectral BSDF-values:
- $BSDF(\theta_i,\varphi_i,\lambda_i,\theta_s,\varphi_s,\lambda_s) = \dfrac{L_{e,\lambda}(\theta_s,\varphi_s,\lambda_s)}{E_{e,\lambda}(\theta_i,\varphi_i,\lambda_i)} = \dfrac{\Phi_{e,\lambda}(\theta_s,\varphi_s,\lambda_s)}{\Phi_{e,\lambda}(\theta_i,\varphi_i,\lambda_i).\Omega_{rec}.|\cos(\alpha_{rec})|}$

- For the full photon budget measurements, the illumination is always perpendicular:

- This allows for a simplification:

  - $BSDF(\lambda_i,\theta_s,\varphi_s,\lambda_s)$

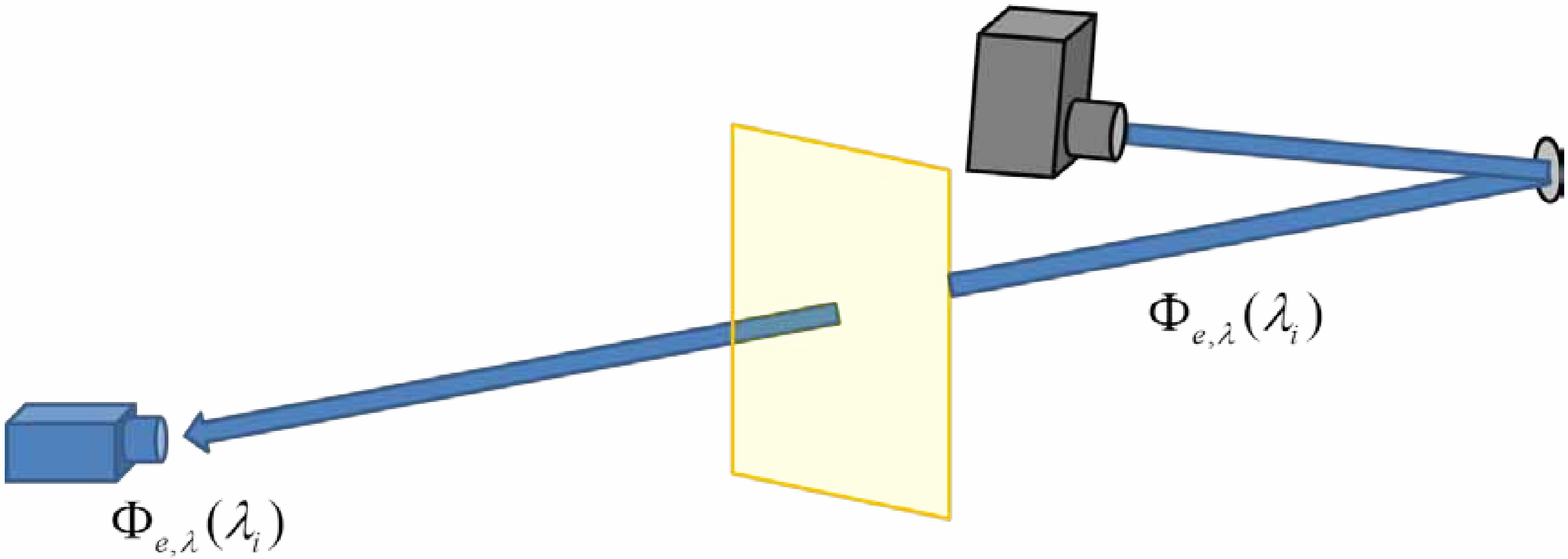
$$= \frac{\Phi_{e,\lambda}(\theta_s,\varphi_s,\lambda_s)}{\Phi_{e,\lambda}(\lambda_i).\Omega_{rec}.|\cos(\alpha_{rec})|}$$



Measurement procedure

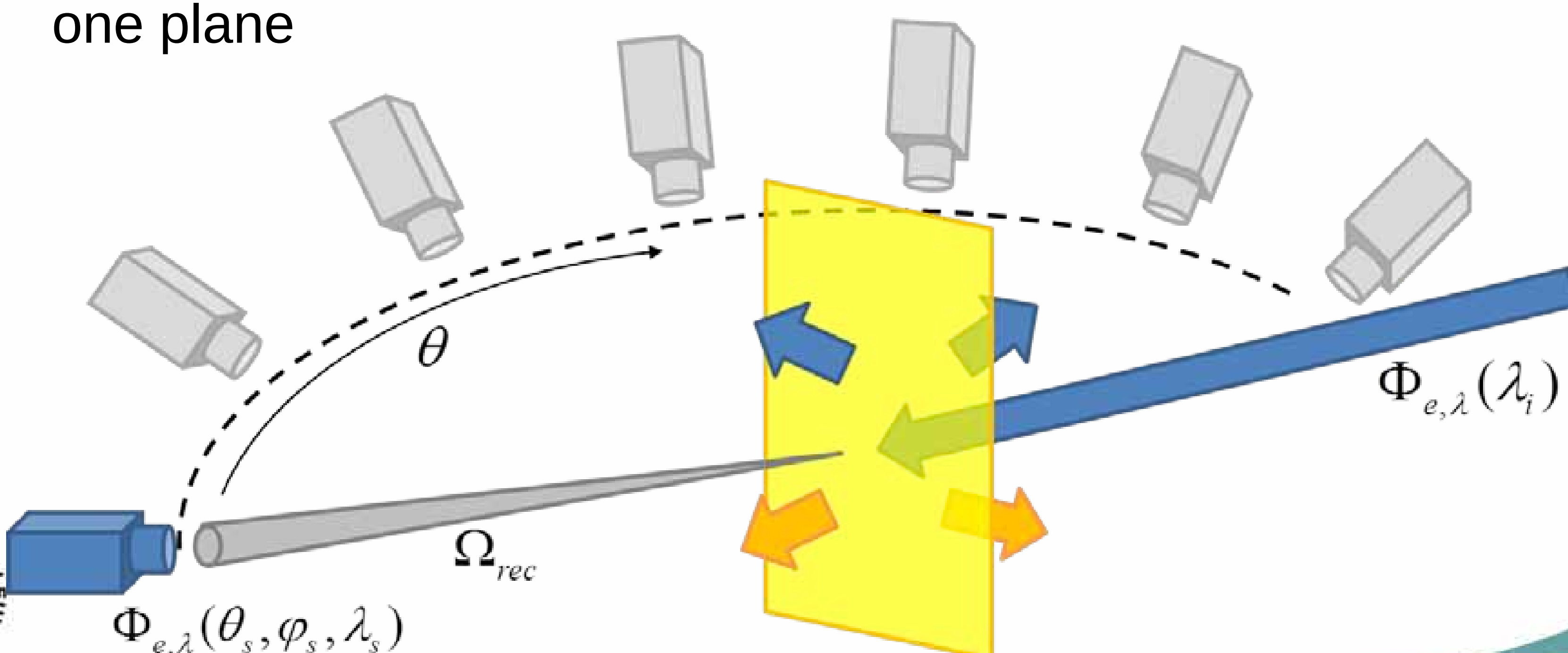
- Step 1: Determination of the incident spectral radiant flux
  - No sample is placed in the sample holder
  - The incident beam enters the detector completely (diameter beam < diameter detector aperture)

    → Measured signal: Incident spectral radiant flux ($\Phi_{e,\lambda}(\lambda_i)$)



Measurement procedure

- Step 2: Measurement of the distributed spectral radiant flux
  - The sample is placed in the sample holder, incident and converted photons are scattered and emitted in all directions
  - The detector head is positioned around the sample
    → Measured signal: Spectral radiant flux within the solid angle subtended from the sample to the detector aperture ($\Phi_{e,\lambda}(\theta_s,\varphi_s,\lambda_s)$)
  - Rotationally symmetric photon distribution → measurements in one plane



Full Photon Budget

- The spectral photon flux can be calculated from the spectral radiant flux with:

$$\Phi_{\lambda}^{ph}(\lambda) = \Phi_{e,\lambda}(\lambda).\frac{\lambda}{h.c}$$

- The full photon budget can be calculated from the spectral BSDF data by integrating over the appropriate wavelength regions for incident and distributed photons and over the appropriate hemisphere:

$$T_{\lambda_{ex} \rightarrow \lambda_{ex}} = \int_{0}^{2.\pi} \int_{\lambda_{ex}} \int_{\lambda_{ex}} BSDF(\lambda_i, \theta_s, \varphi_s, \lambda_s).\lambda_i / \lambda_s.|\cos(\alpha_{rec})|.d\lambda_s.d\lambda_i.d\Omega$$

$$= 2.\pi \int_{0}^{\pi/2} \int_{\lambda_{ex}} \int_{\lambda_{ex}} BSDF(\lambda_i, \theta_s, \varphi_s, \lambda_s).\lambda_i / \lambda_s.|\cos(\alpha_{rec})|.\sin(\theta_s).d\lambda_s.d\lambda_i.d\theta_s$$

Full Photon Budget

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- Similar calculations for:
  - Pct of photons scattered in reflection ($R_{\lambda_{ex} \rightarrow \lambda_{ex}}$)
  - Pct of converted and emitted photon in forward direction ($T_{\lambda_{ex} \rightarrow \lambda_{em}}$)
  - Pct of converted photon/s in backward direction ($R_{\lambda_{ex} \rightarrow \lambda_{em}}$)
- And finally, the pct of photons lost can be calculated:
  - $L_{\lambda_{ex}} = 1 - (T_{\lambda_{ex} \rightarrow \lambda_{ex}} + R_{\lambda_{ex} \rightarrow \lambda_{ex}} + T_{\lambda_{ex} \rightarrow \lambda_{em}} + R_{\lambda_{ex} \rightarrow \lambda_{em}})$

- Similar calculations when the sample is illuminated with the emission wavelength

Validation

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- Two reference samples were measured (non-fluorescent):
  - A gray reflection standard (calibrated by NPL)
  - A white reflection standard (calibrated by NPL)

- Measured value: $R_{\lambda_{ex} \rightarrow \lambda_{ex}}$

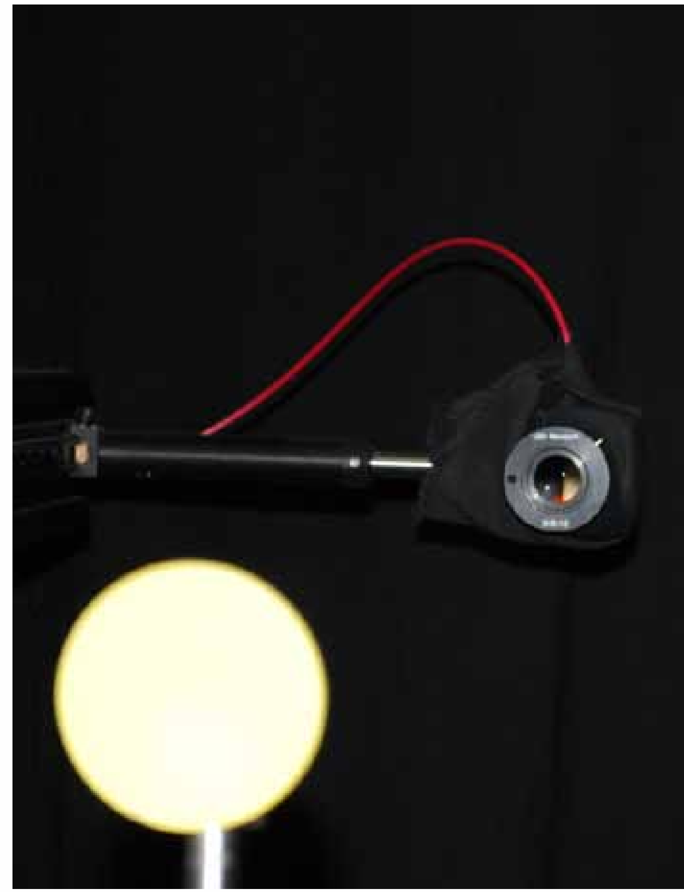
- Results:

	Calibration value	Measured value
White reference	0.96	0.96
Gray reference	0.30	0.29

Experimental results

- The full photon budget of a commercial remote phosphor component was measured:
- $\lambda_{ex} = 460$ nm; $\lambda_{em} = 580$ nm

Full photon budget	
$T_{\lambda_{ex} \rightarrow \lambda_{ex}}$	10.7 %
$R_{\lambda_{ex} \rightarrow \lambda_{ex}}$	6.3 %
$T_{\lambda_{ex} \rightarrow \lambda_{em}}$	35.1 %
$R_{\lambda_{ex} \rightarrow \lambda_{em}}$	40.4 %
$L_{\lambda_{ex}}$	7.5 %
$T_{\lambda_{em} \rightarrow \lambda_{em}}$	43.0 %
$R_{\lambda_{em} \rightarrow \lambda_{em}}$	51.1 %
$L_{\lambda_{em}}$	5.9 %



Experimental results

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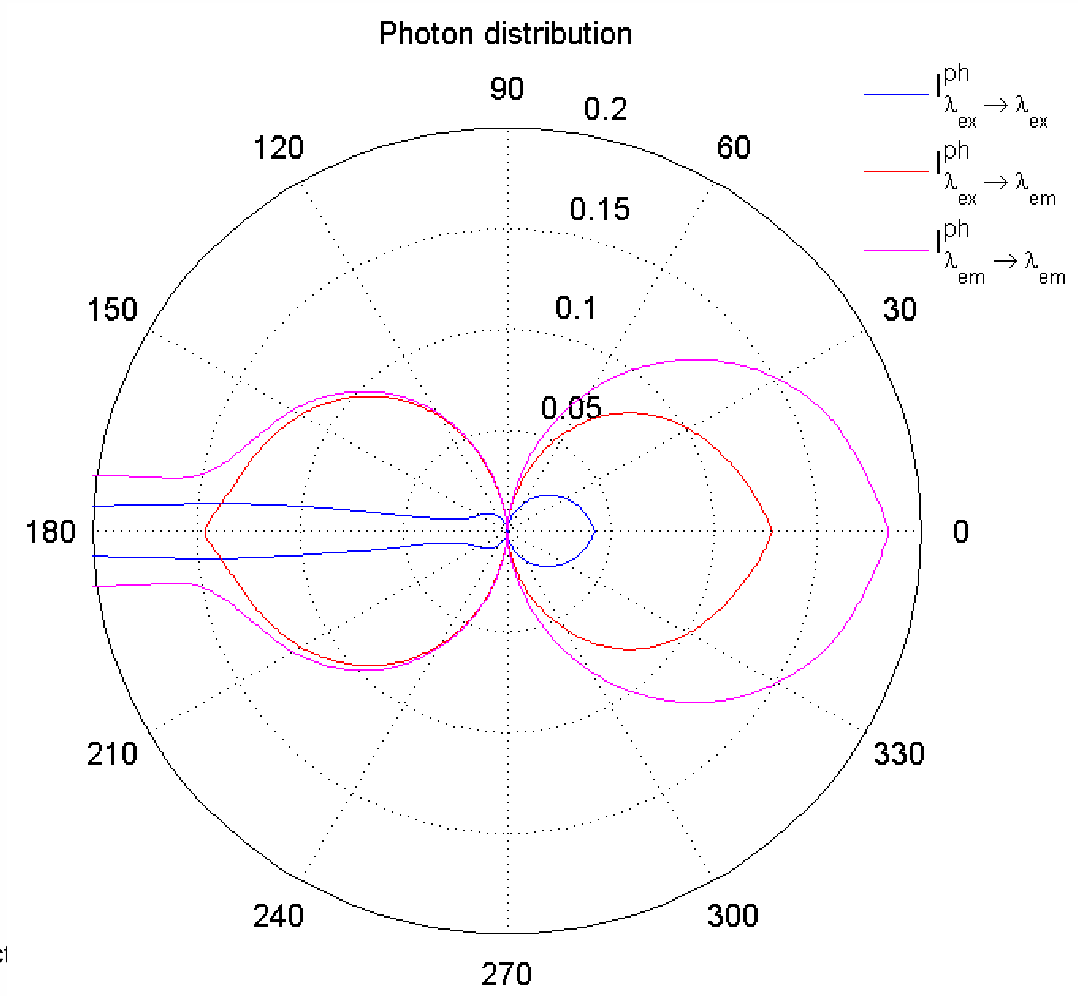
- From the spectral BSDF-values, the spatial photon intensity distribution can be drawn:



Experimental results

- First interaction with the phosphor component:
  - A large portion of the non-converted incident photons is reflected back toward the light source (37.0 %)
  - More than half (53.5 %) of the converted photons are emitted back towards the source
- Second and following interactions of converted photons with the phosphor component:
  - More than half (54.3 %) of the photons are reflected back towards the light source (again)

- Further research:
  - Higher extraction efficiency of the photons
  - Higher recycling efficiency of the backward directed photons

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Questions?

Thank you for your attention!