Integrating Sphere Measurements; reflection, transmission, and absolute quantum yield

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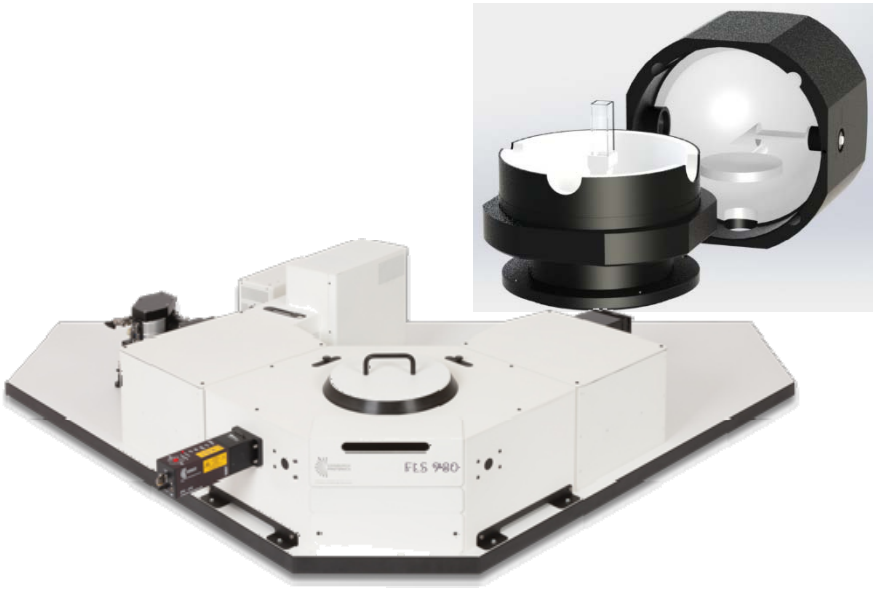
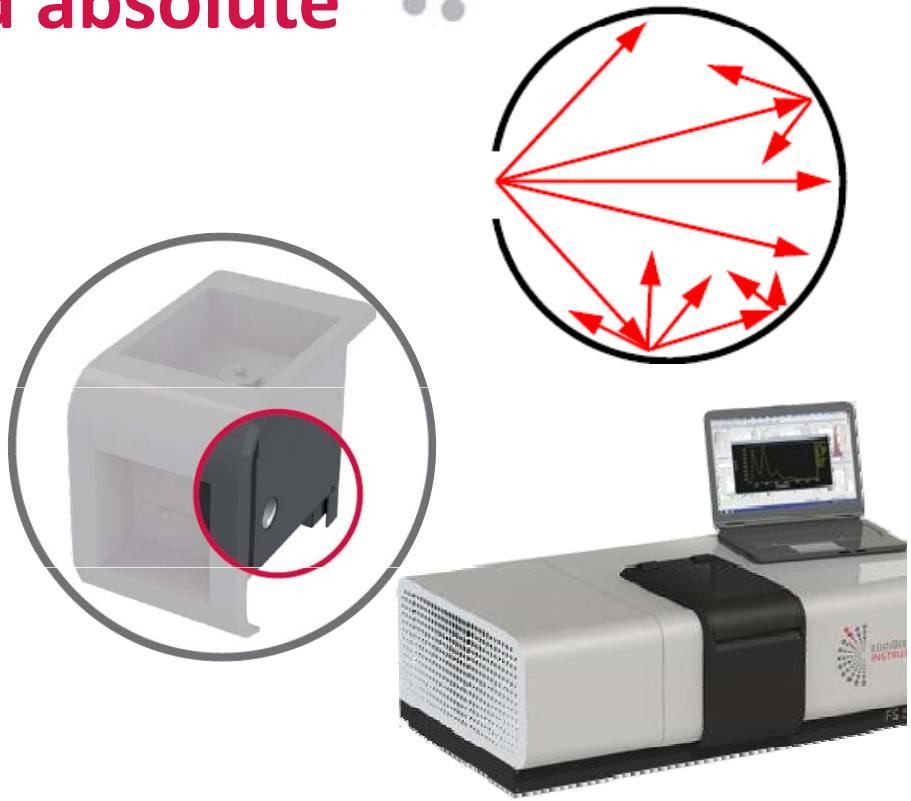


The FLS980 Research Grade Steady State & Lifetime Fluorescence Spectrometer



The FS5 Analystical Grade Steady State & Lifetime Fluorescence Spectrometer

Pride in precision

What is an Integrating Sphere ?

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- **An integrating sphere is an optical device that can be used in a spectrometer for measuring various parameter including:**

  - ✓ **Optical flux from a light source**
  - ✓ **Scattering losses / reflection from a surface**
  - ✓ **Fluorescence quantum yields**

Integrating Sphere:

Design Considerations

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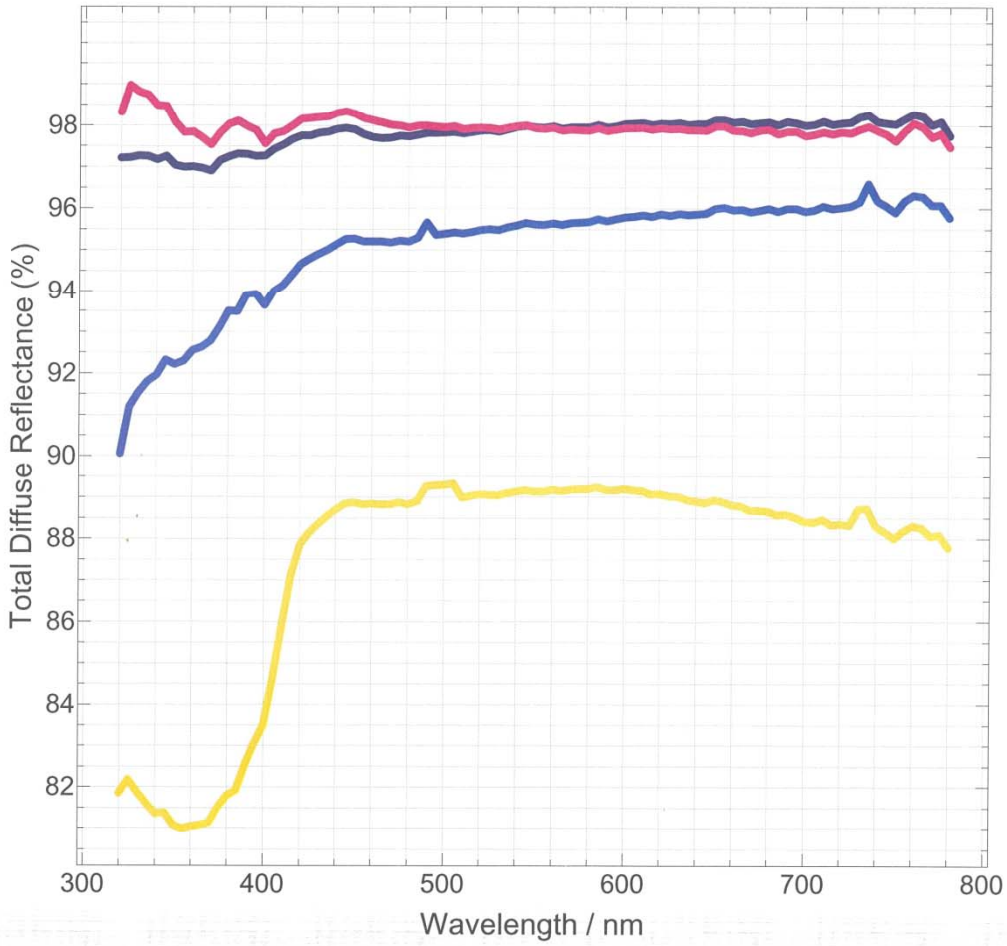
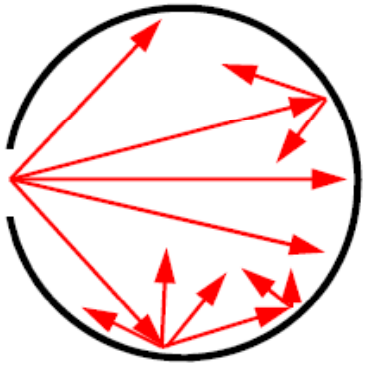
- The quality of measurements performed with integrating spheres strongly depends on the:
  - sphere's coating material
  - exact position of baffles
  - size of the ports in relation to sphere's diameter
  - correction of light and signal responses

Integrating Sphere:
Materials for High Reflectivity



- Opdima
- Spectralon
- **Benflect**
- $BaSO_4$



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What is an Integrating Sphere ?

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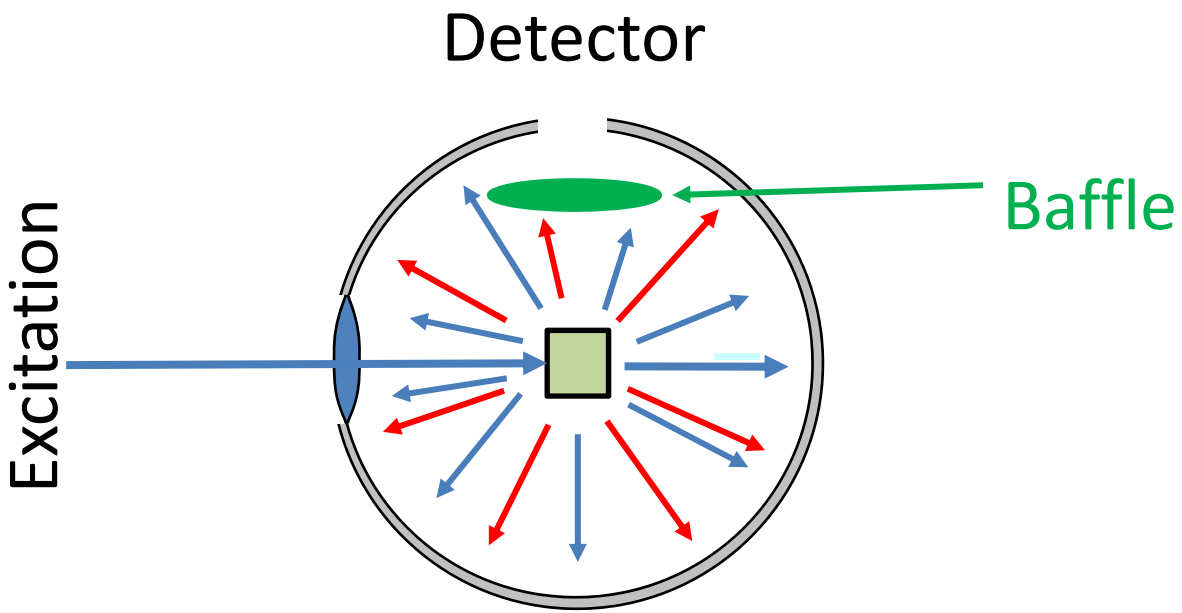
Theory states that every photon must bounce at least twice before exiting to homogenize the directional signal

→ Baffle placement is very important!



Integrating Sphere:
Corrected Response

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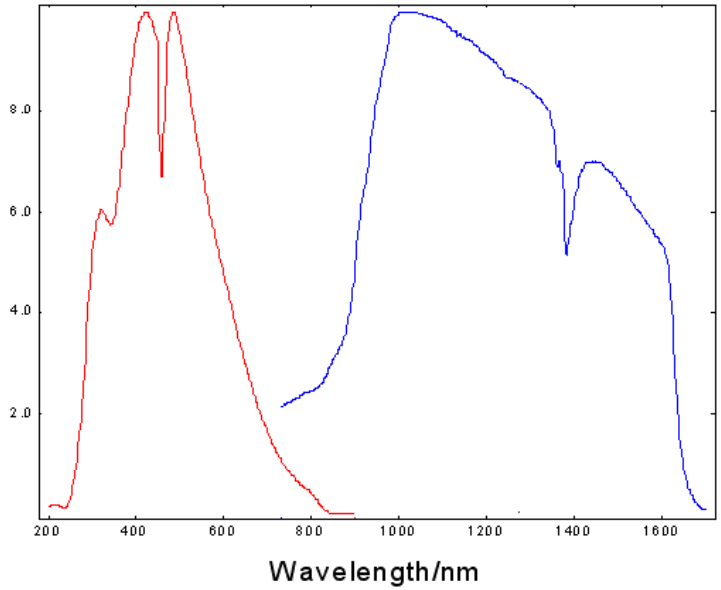
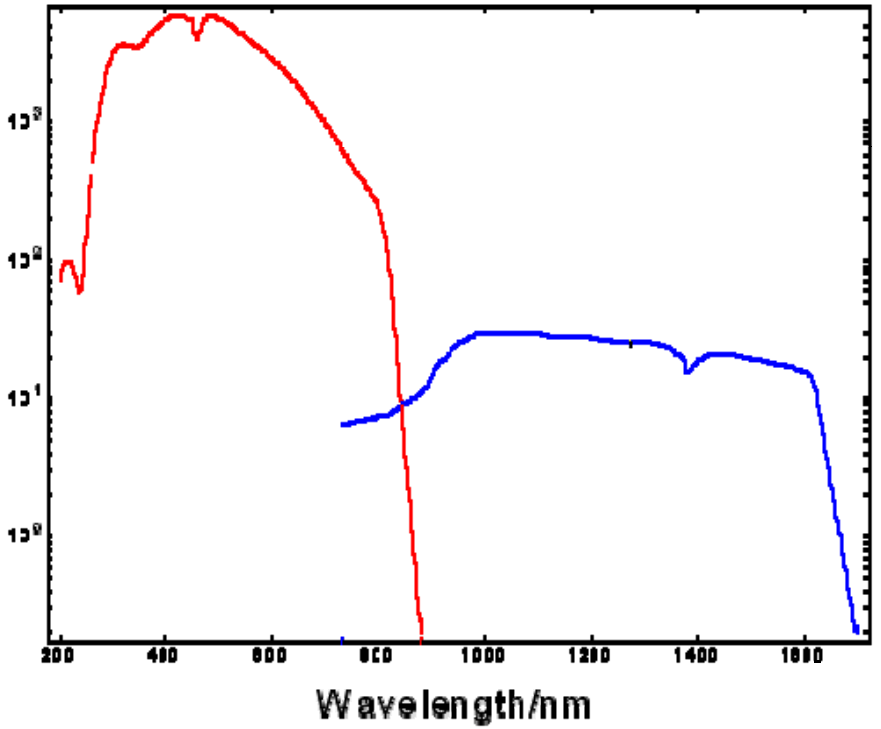
Normalized Detector Q.E.



Corrected Detector Response



Without correction – results are *very wrong*!

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Integrating Sphere:
Other Examples

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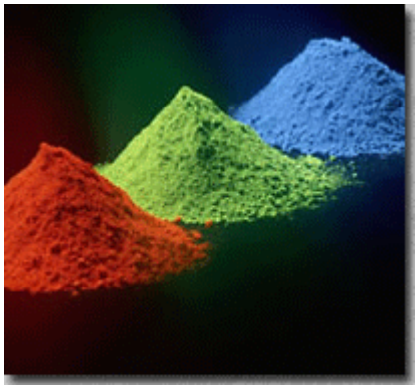
Testing for new phosphors…



… to car head-lights and solid-state lighting…

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Integrating Sphere:
Edinburgh Instruments Designs

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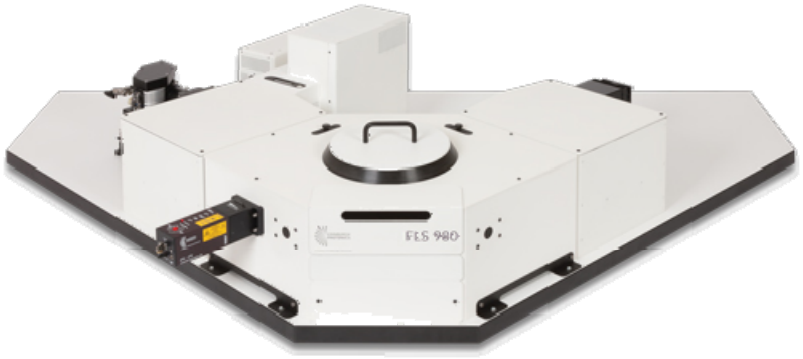

The FLS980 Research Grade Steady State & Lifetime Fluorescence Spectrometer

The FS5 Analystical Grade Steady State & Lifetime Fluorescence Spectrometer

Pride in precision

Integrating Sphere:

FLS980

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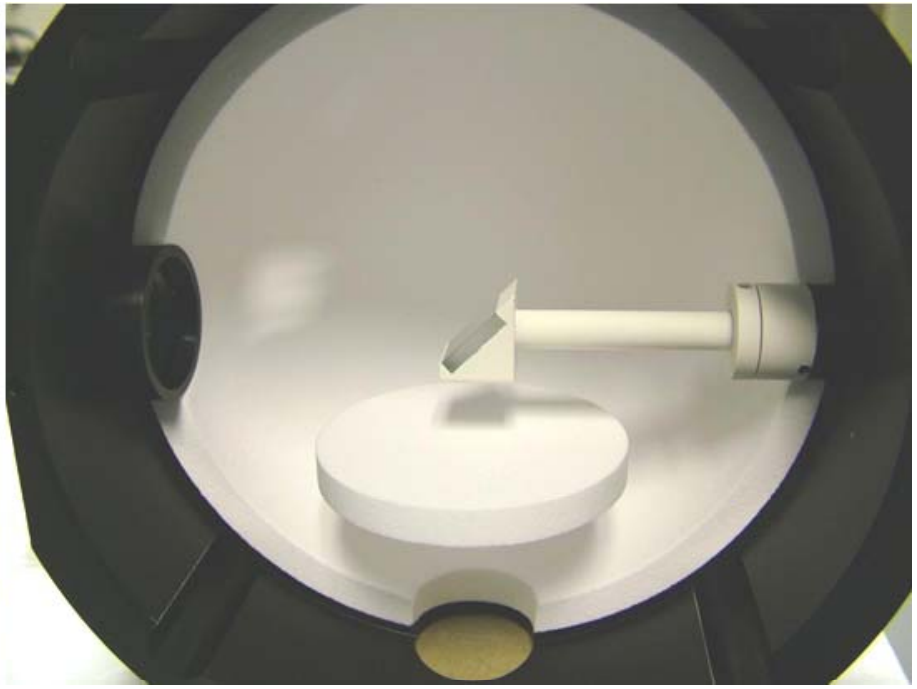
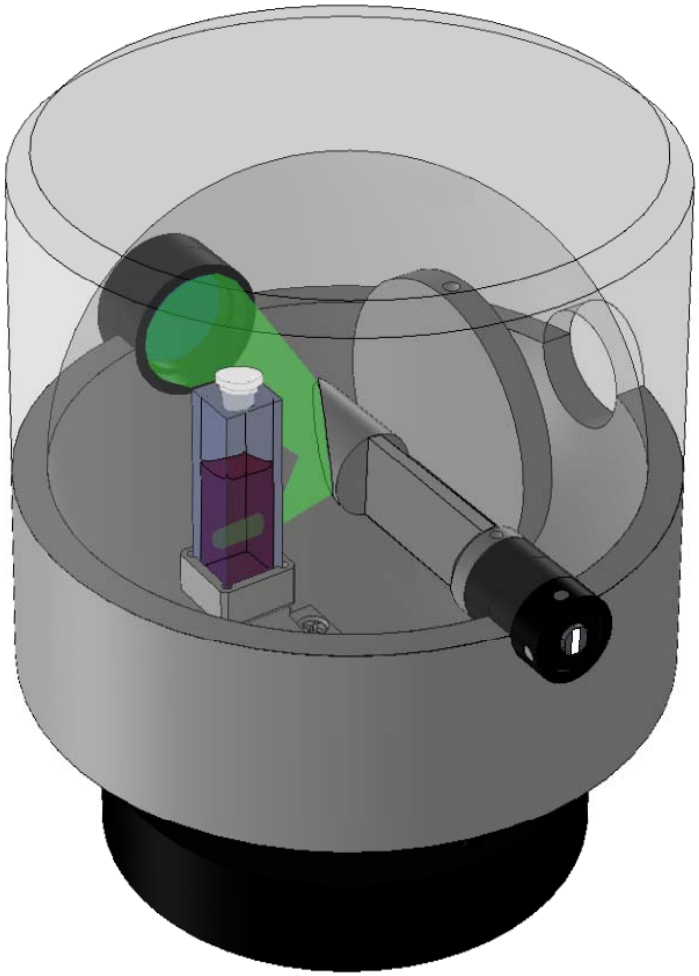


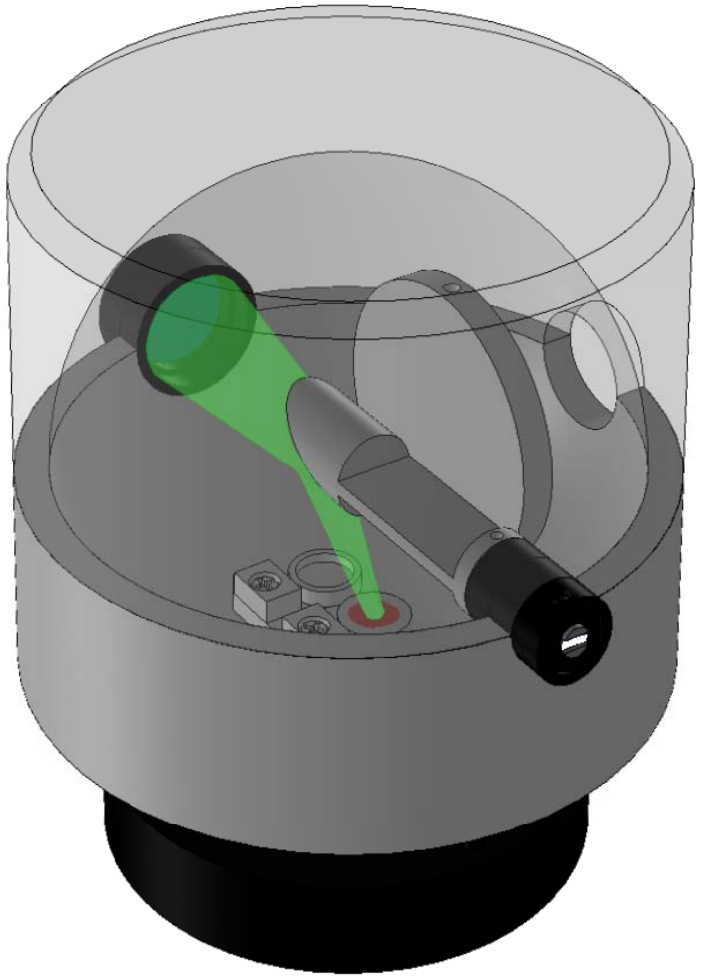
Mirror, baffle, lens and filter holder embedded in top half to allow easy access for sample exchange.

Integrating Sphere:

FLS980



Solution



Solid

Integrating Sphere:

FS5 SC-30 Integrating Sphere Module

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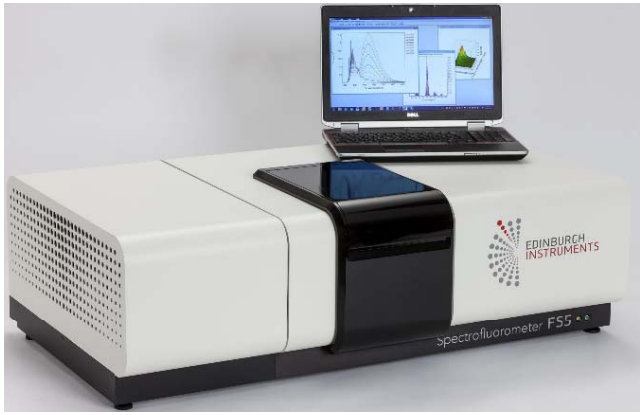

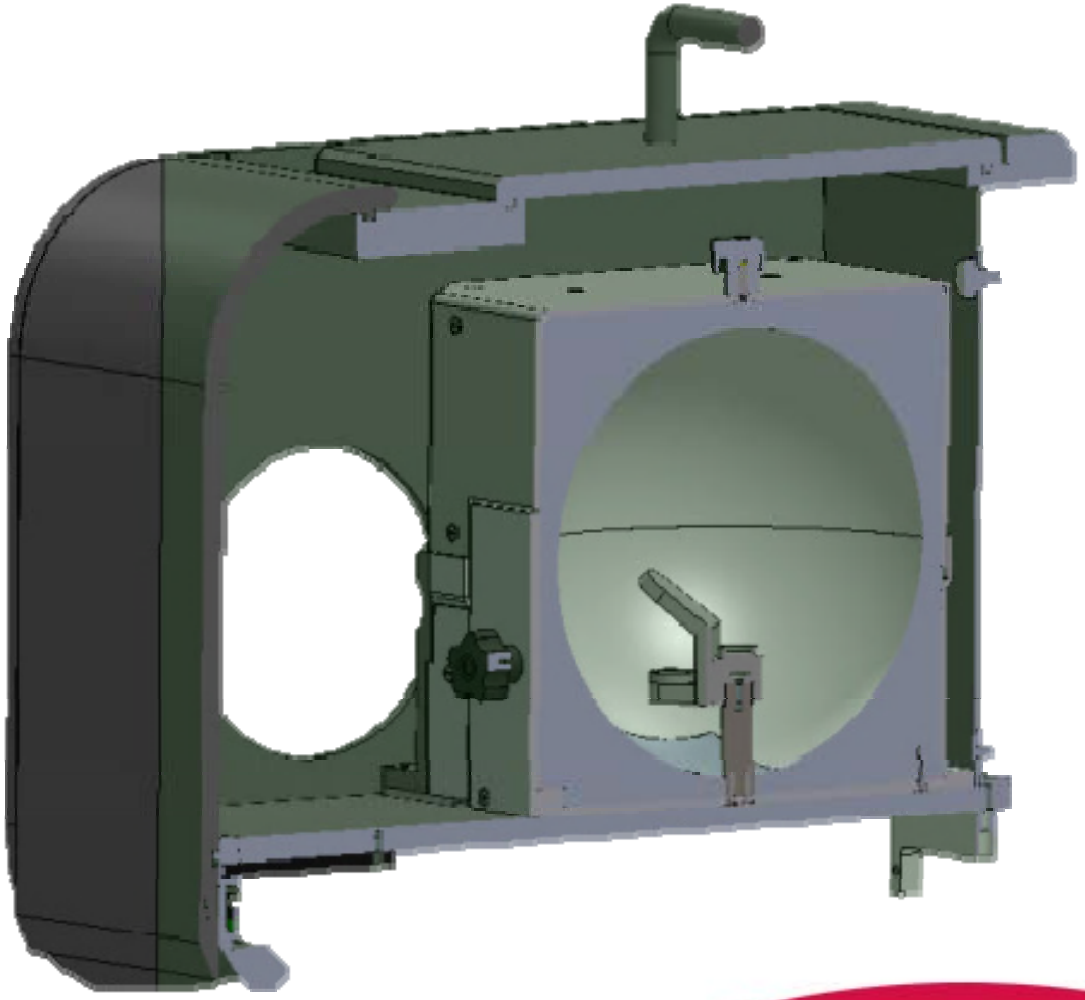

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Integrating Sphere Measurements:
Reflectance / Absorbance

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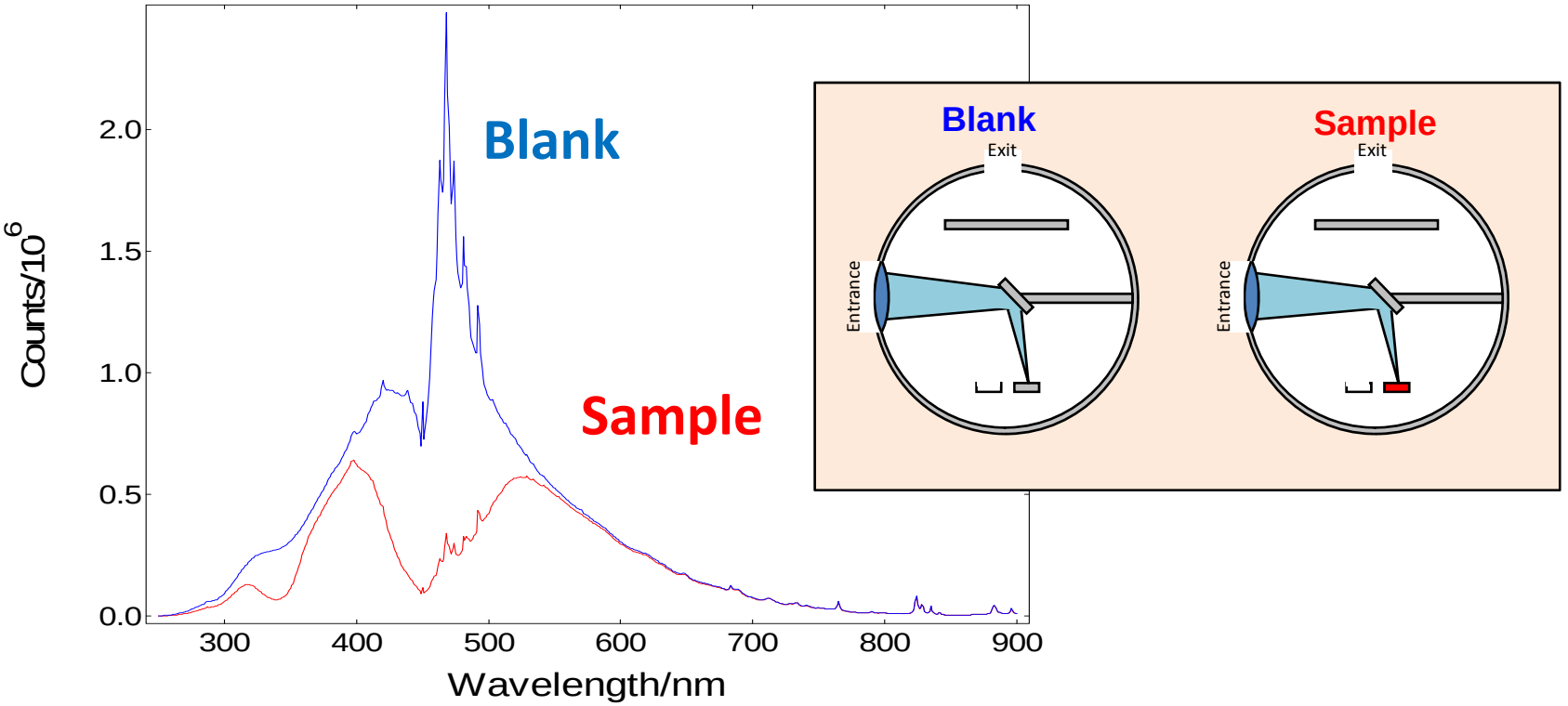
Reflectance / Absorbance Measurements of Opaque Samples

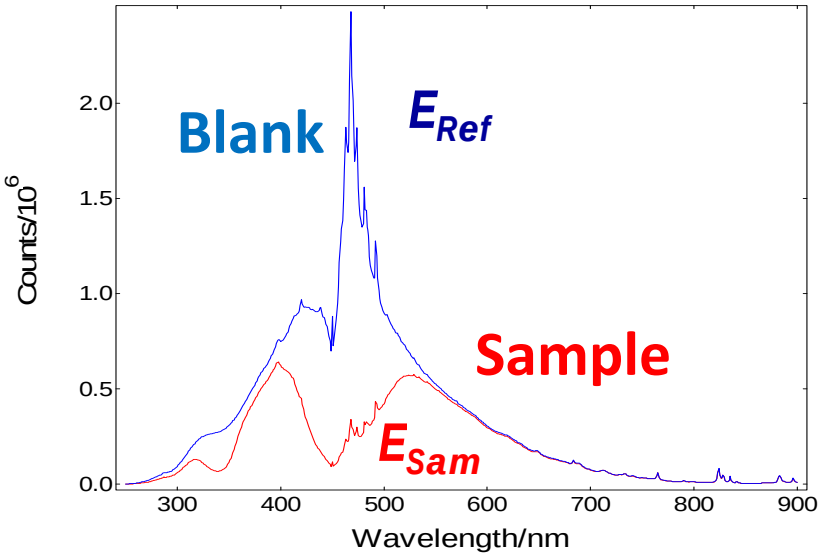


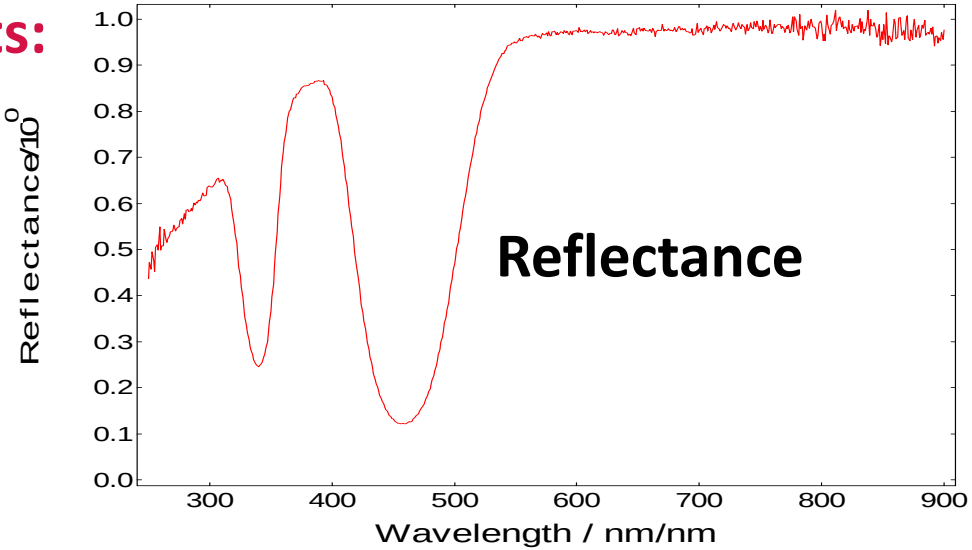
Utilizing a synchronous scan of a scattering "Blank" and compare it with sample

Integrating Sphere Measurements:

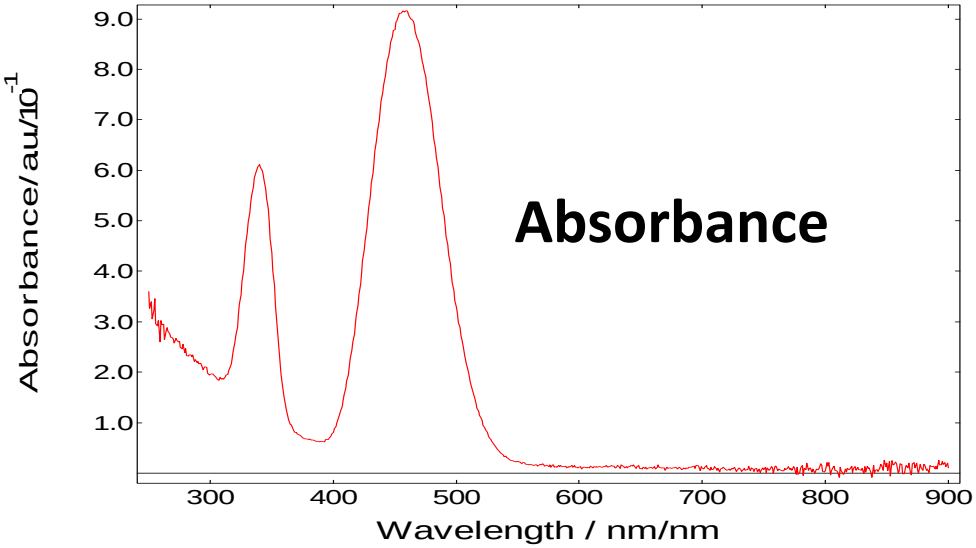
Reflectance / Absorbance

$$R(\lambda) = \frac{E_{Sam}(\lambda)}{E_{Ref}(\lambda)}$$





$$A(\lambda) = Log_{10}\frac{E_{Ref}(\lambda)}{E_{Sam}(\lambda)}$$



Integrating Sphere Measurements:
Photoluminescence Quantum Yield

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Absolute (Sphere)

- DIRECT measurement
- Applicable for all type of samples
- More accurate
- Can be performed over a wide spectral range

Relative

- Requires known standard that has similar spectral characteristics
- Relies on the known standard's value being correct
- Requires multiple tedious measurements

Integrating Sphere Measurements: PLQY Principle

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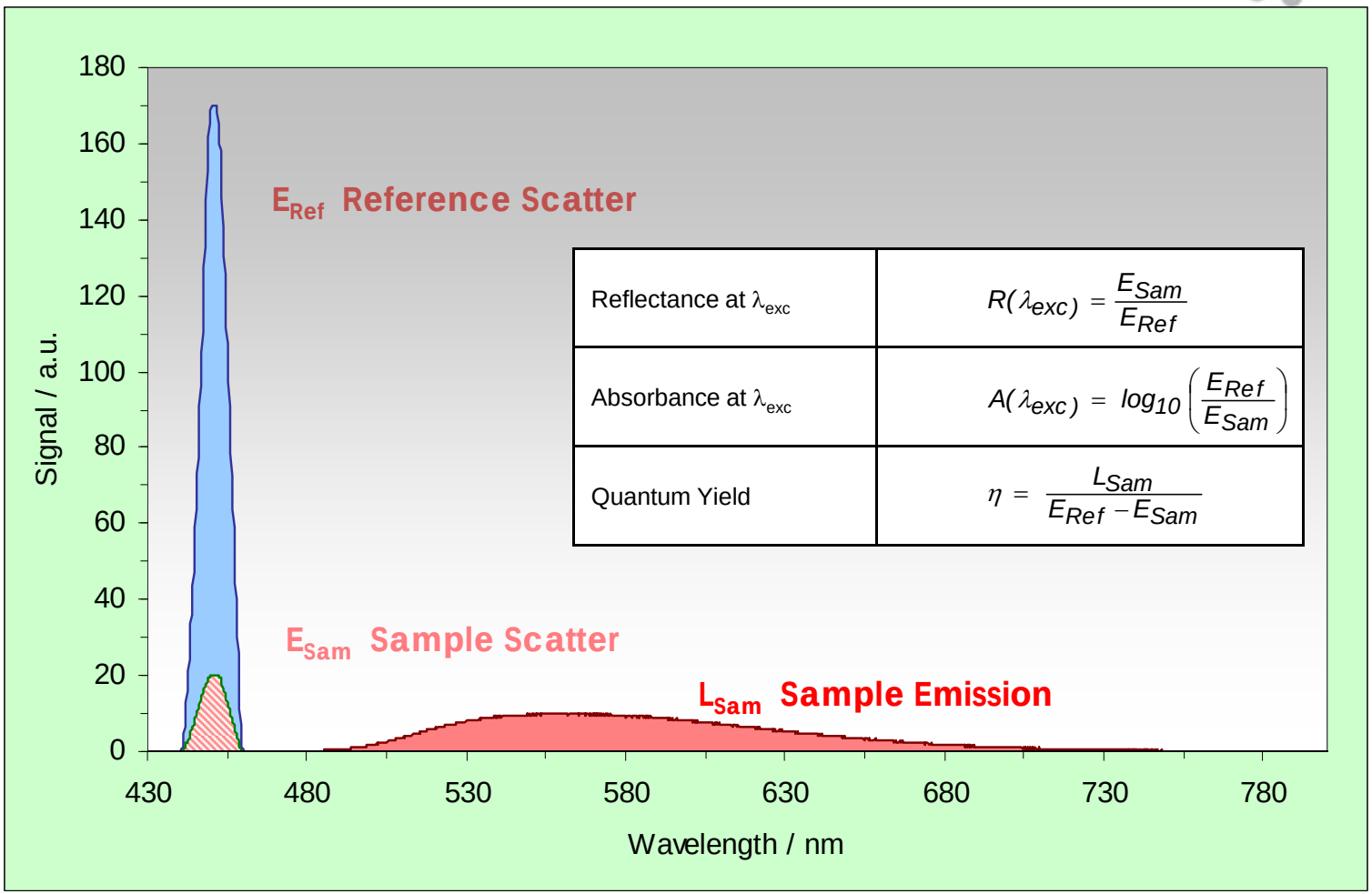
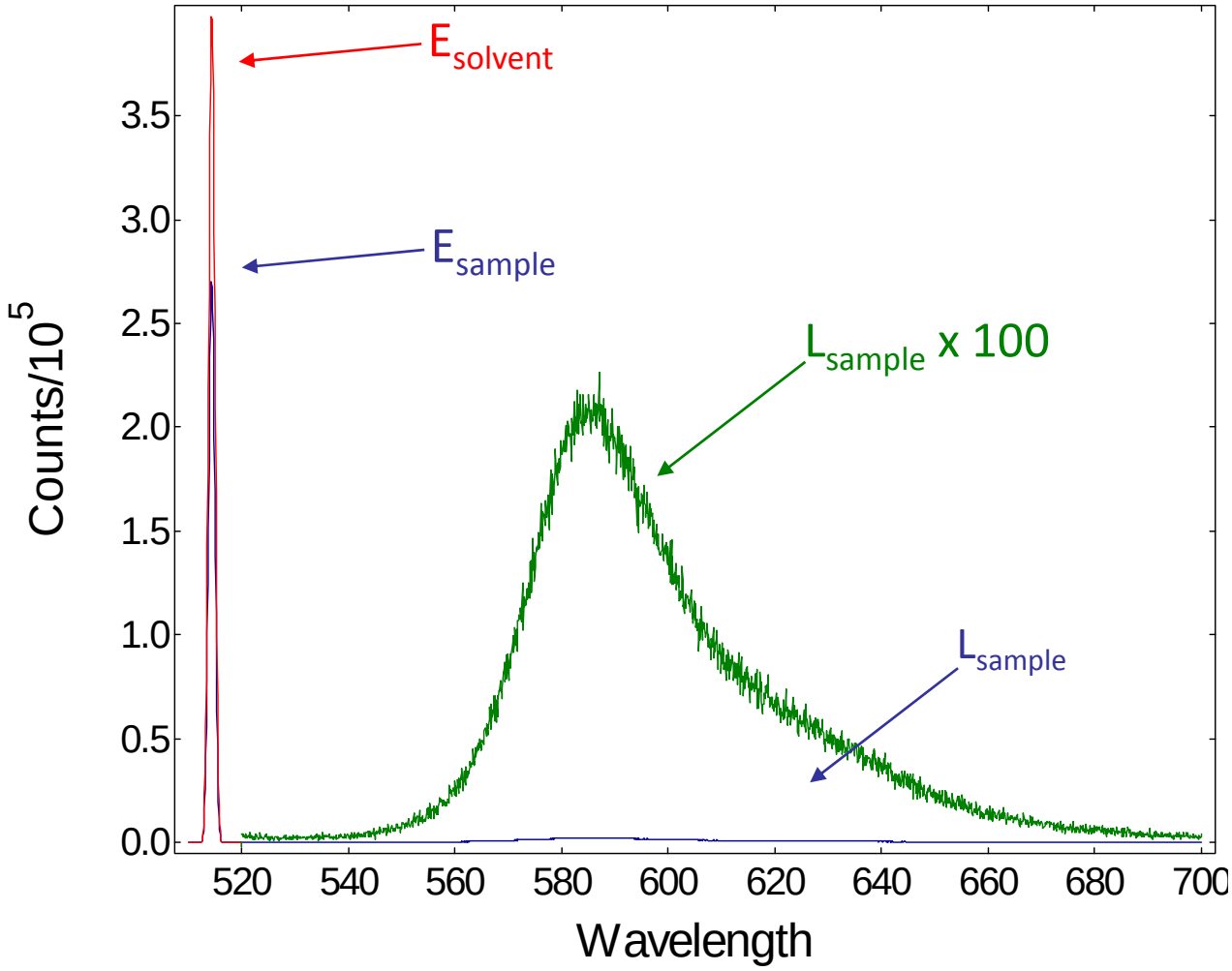


Reflectance at λ_{exc}	$R(\lambda_{exc}) = \frac{E_{Sam}}{E_{Ref}}$
Absorbance at λ_{exc}	$A(\lambda_{exc}) = log_{10}\left(\frac{E_{Ref}}{E_{Sam}}\right)$
Quantum Yield	$\eta = \frac{L_{Sam}}{E_{Ref} - E_{Sam}}$

Integrating Sphere Measurements: PLQY Measurement Examples



DIRECT measurement

Applicable for all type of samples

-Weak Emitters

-Strong Emitters

-UV emitters

-NIR Emitters

-Solids, Solutions, Films

Pride in precision

Integrating Sphere Measurements:

Wavelength Independent PLQY

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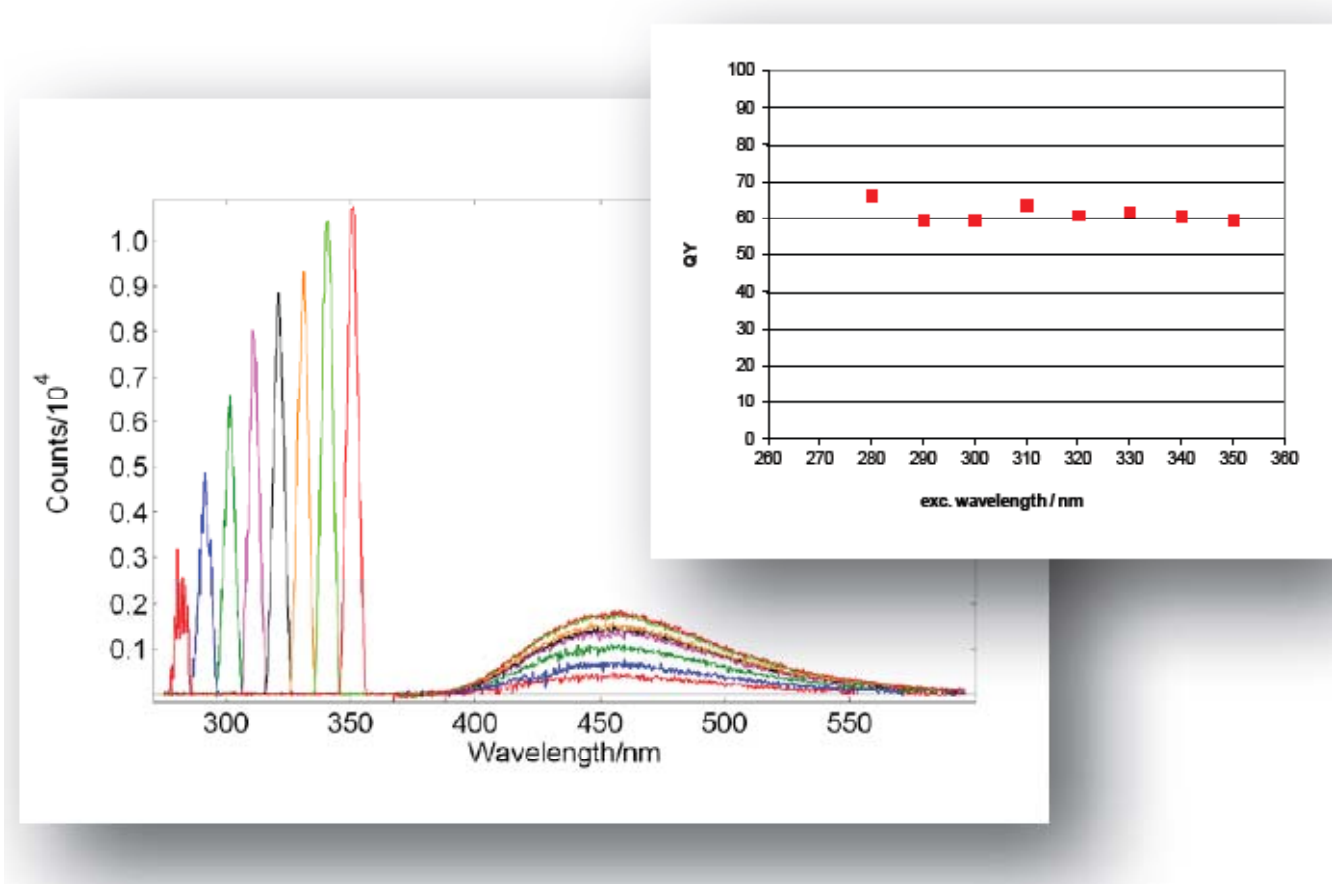
Independence of the fluorescence quantum yield from the wavelength of excitation for a standard organic dye.



Left - area of absorption for 7 different excitation wavelengths (i.e. blank scatter minus sample scatter)

Right the corresponding 7 emission spectra, scaled by a factor of 5 for better visualisation.

Integrating Sphere Measurements:

Rhodamine 6G in ethanol

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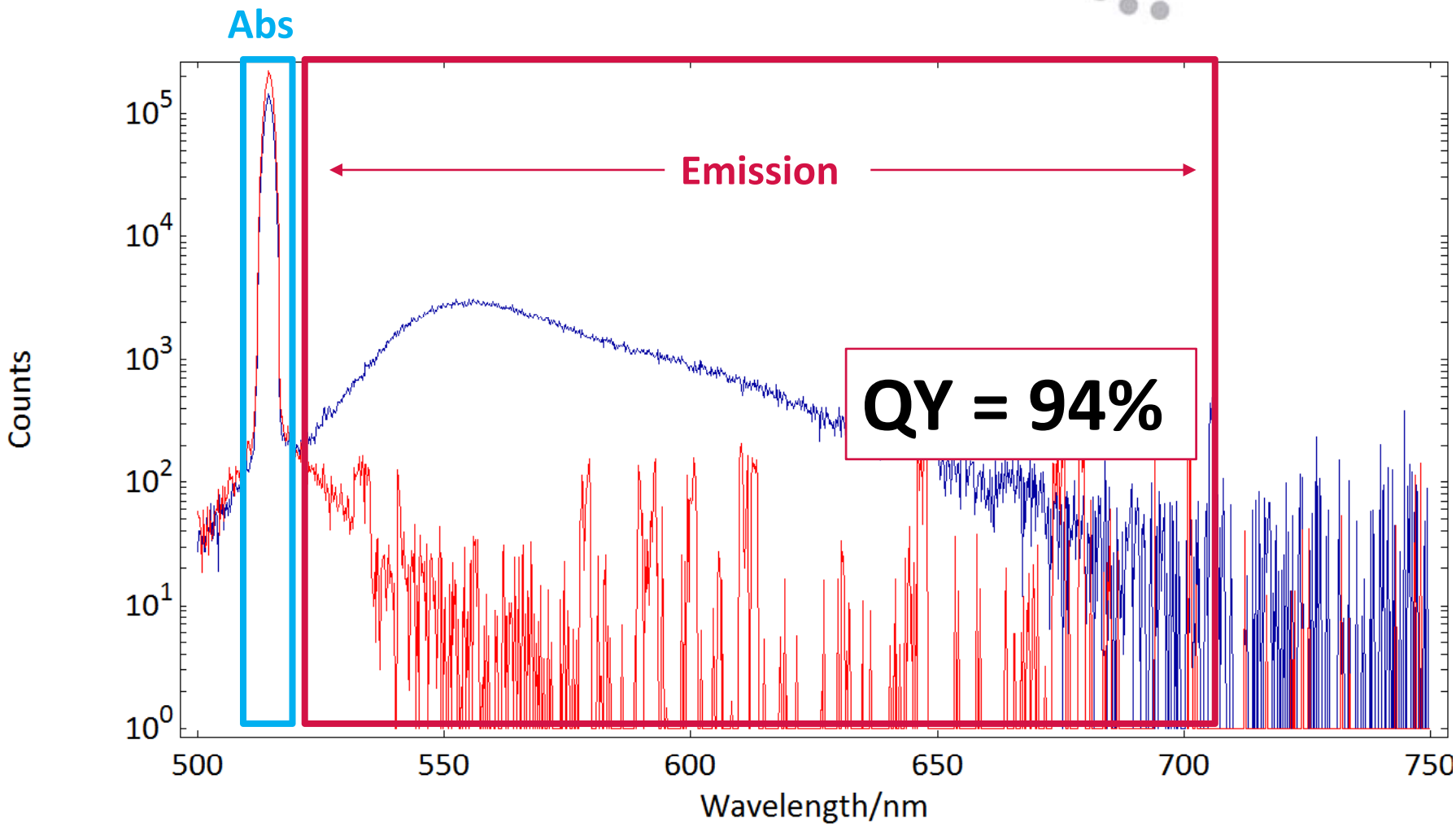

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Integrating Sphere Measurements:

Rare-earths in the NIR

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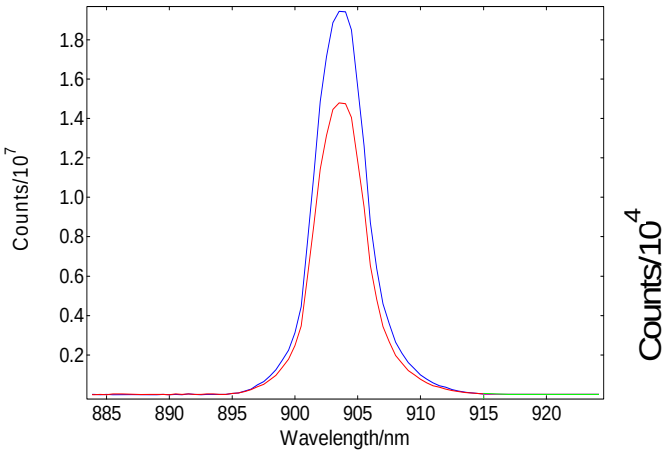
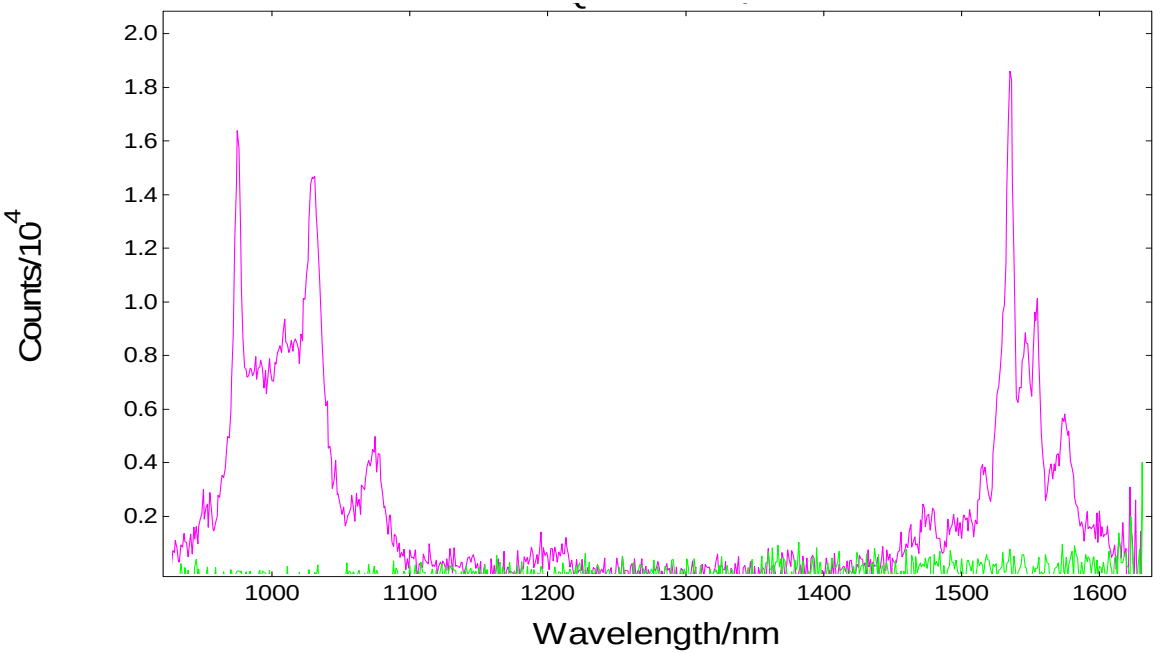
Y_2O_3 sensitised with Yb and doped/codoped with rare-earth ions





$QY_{927\text{-}1150nm}$= 4.0 ± 0.2 % $QY_{1400\text{-}1625nm}$= 2.5 ± 0.1 % $QY_{927\text{-}1625nm}$= 6.9 ± 0.4 %

λ_{exc} = 907nm 0.5nm step for scattering peaks and 1 nm for emission

$\Delta\lambda_{exc}$ = 10nm, $\Delta\lambda_{em}$ = 3.5nm, 2s integration time

ND1 filter used when measuring the scattered light to avoid detector saturation

Rare-Earth Upconversion Luminescence

980 nm Laser Mounting to FLS980

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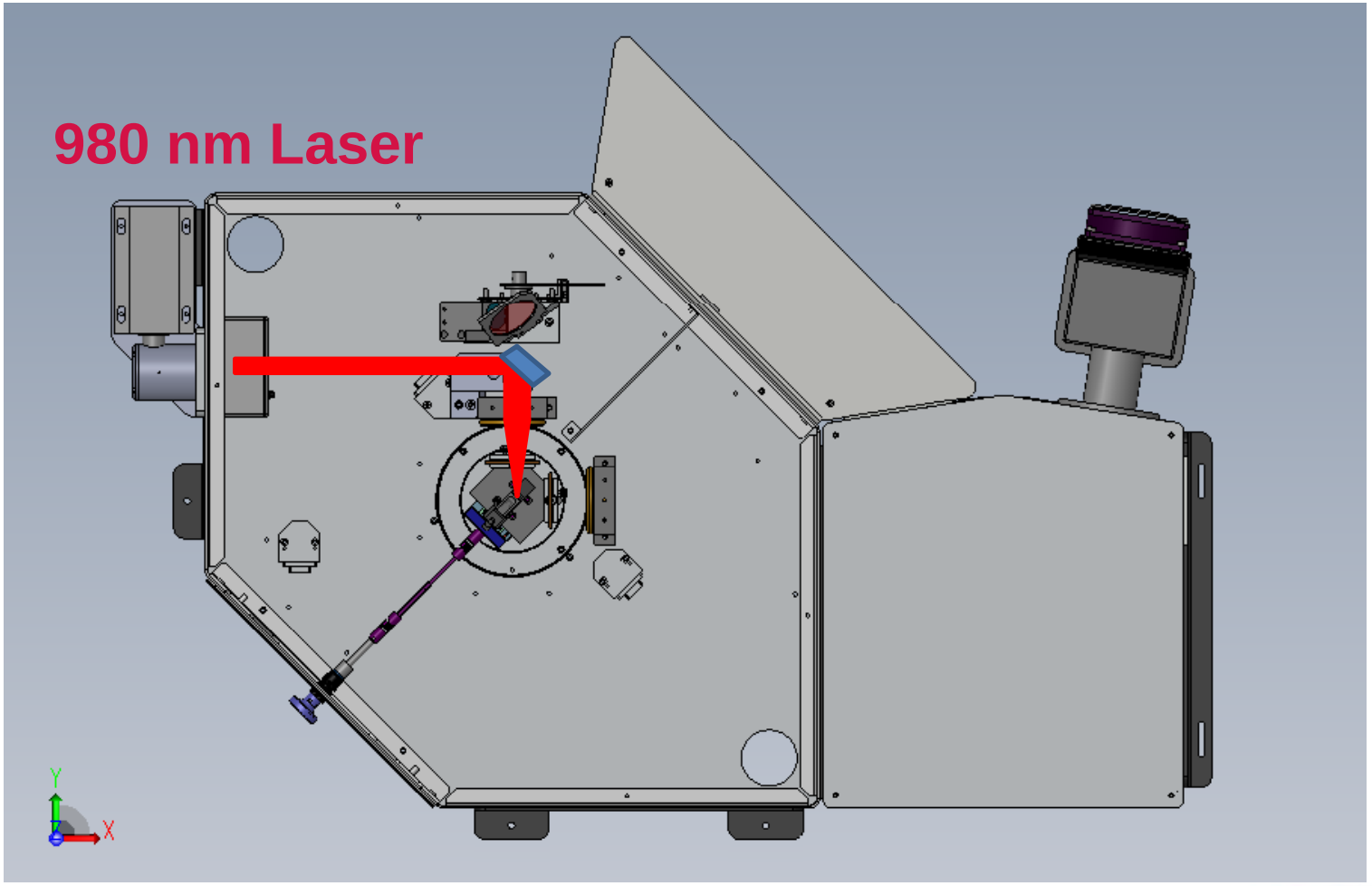
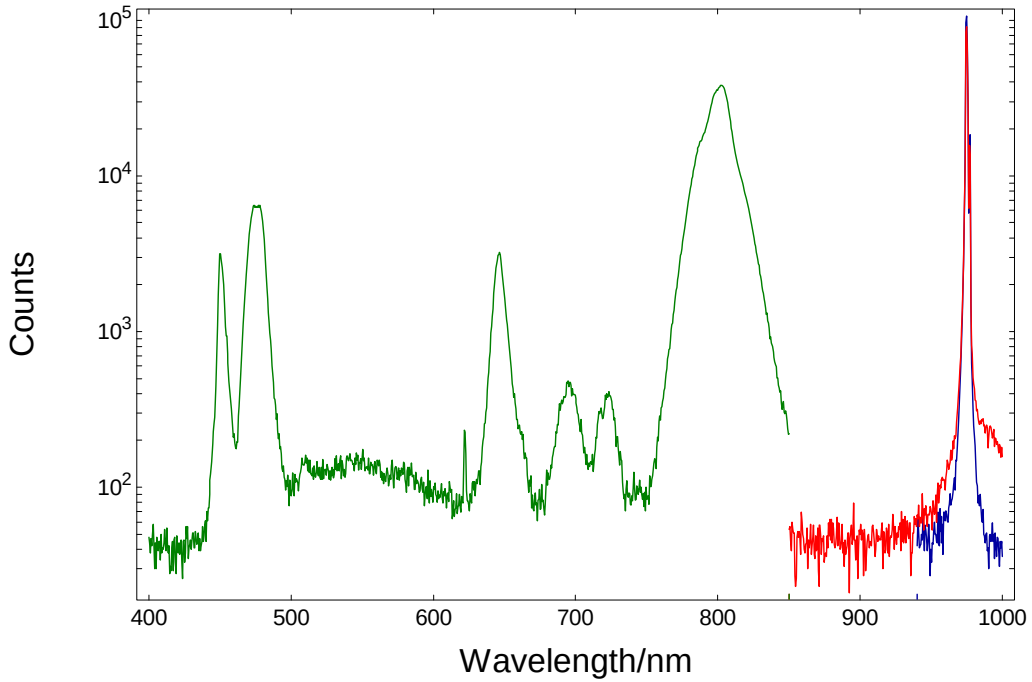


Rare-Earth Upconversion Luminescence

Quantum Yield Measurement



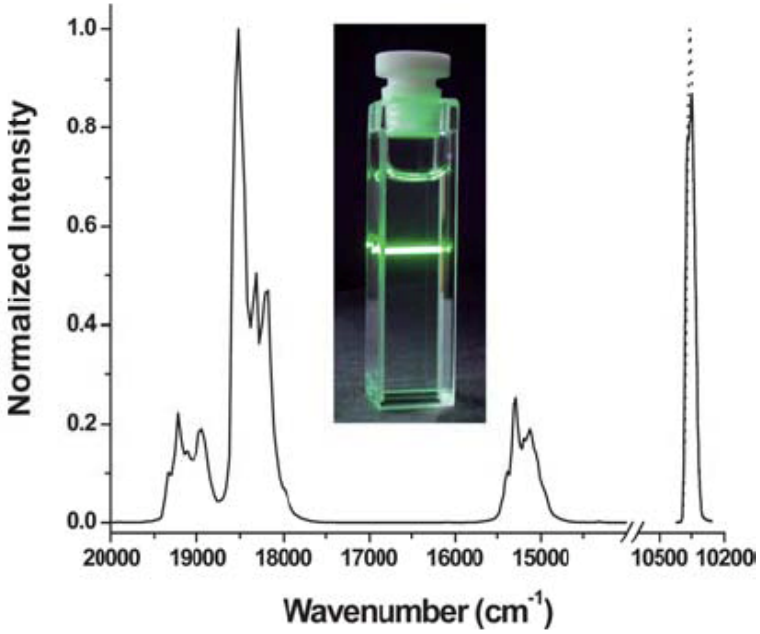
Blue – scattering peak of the reference material;
Red – scattering peak of the sample;
Green – emission from the sample.

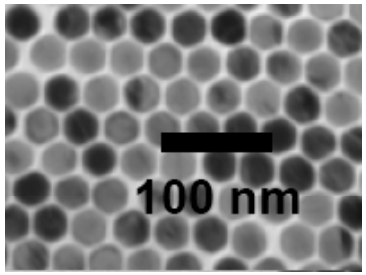
Evaluated value of quantum yield was 3%.

100 mW of laser power.
Benflect plug was used as a reference.
Measurement parameters were: step – 0.5 nm, $\Delta\lambda_{em}$ – 0.5 nm, integration time – 0.5 sec.
Scattering peaks were measured using 0.1 %T neutral density filter, so for quantum yield calculation these peaks were scaled up by factor 1000.
Evaluated value of quantum yield was 3 %.

Rare-Earth Upconversion Luminescence

Quantum Yield Measurement





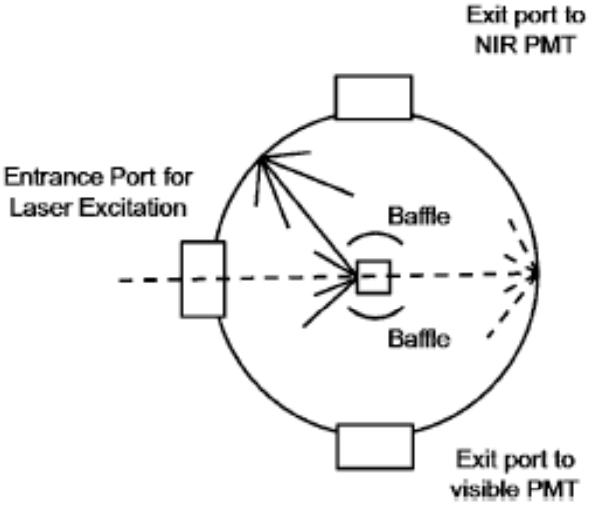


Table 1 QYs of the NaYF4: Er^{3+} 2%, Yb^{3+} 20% samples

Sample #	Average particle size/nm	Power density/ W cm^{-2}	QY (%)
ErYb1	≫100	20	3.0 ± 0.3
ErYb2 (1 wt%)	100	150	0.30 ± 0.10
ErYb3 (1 wt%)	30	150	0.10 ± 0.05
ErYb4 (1 wt%)	8–10	150	0.005 ± 0.005
ErYb5 core shell (1 wt%)	30	150	0.30 ± 0.10

Boyer, J. C.; van Veggel, F. Nanoscale 2010, 2, 1417-1419.

Integrating Sphere:
Summary

EDINBURGH INSTRUMENTS

Direct measurement of Reflectance / Absorbance

Direct measurement of Photoluminescence Quantum Yield

Applicable for:

-Weak Emitters

-Strong Emitters

-UV emitters

-NIR Emitters

-Solids, Solutions, Films