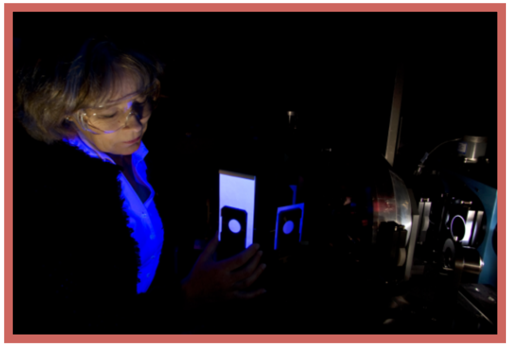
Improving Traceability of Fluorescence Calibrations to Practical Colorimetric Applications



9th Biannual Joint US/CIE and CNC/CIE Technical Day
7 November 2013

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Measurement Science and Standards
National Research Council of Canada

Traceability

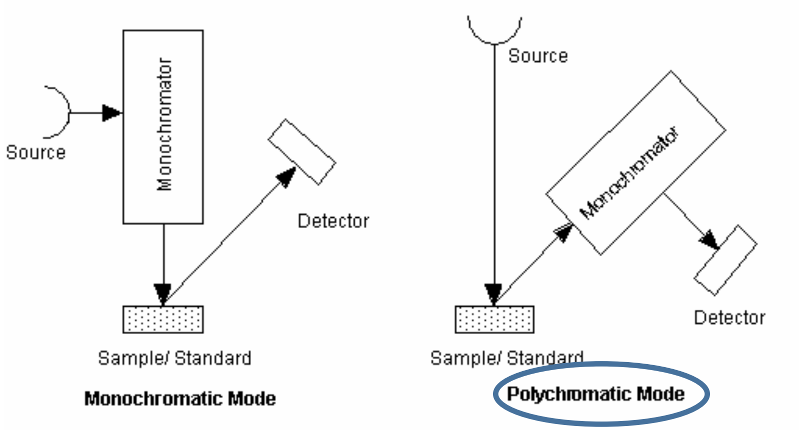
Property of the result of a measurement whereby it can be related to stated references, usually national or international standards, by an ***unbroken chain of comparisons*** all having ***stated uncertainties*** [VIM 6.10]

Traceable calibrations must have ***stated uncertainties*** and a "***traceability chain***"

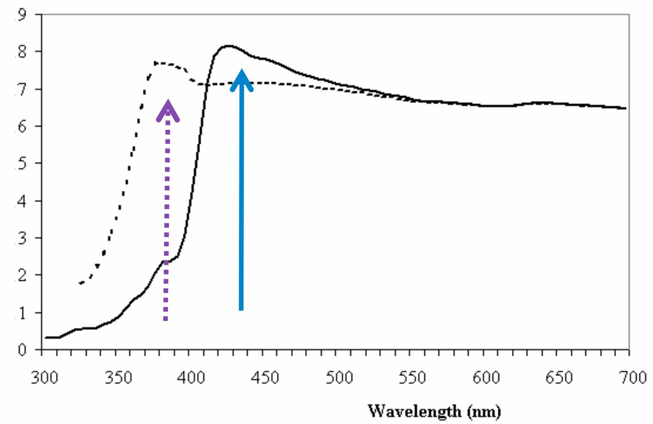
Fluorescence Instrumentation

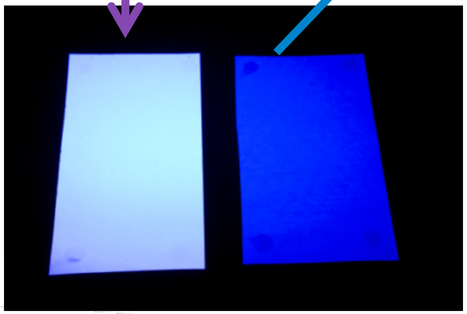
Conventional Spectrophotometer

One Monochromator Methods



Fluorescent Sample
Mono vs Poly mode



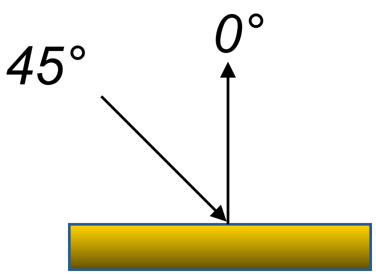


Mono mode:
Meaningles colorimetric results!!

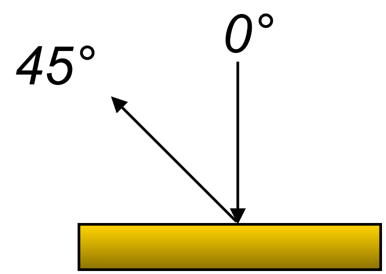
CIE Reflectance Geometries

Illumination/ Viewing

Bidirectional



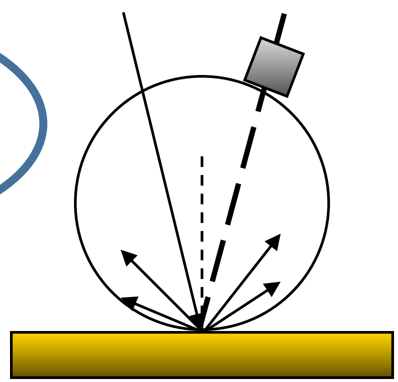
45°:0°



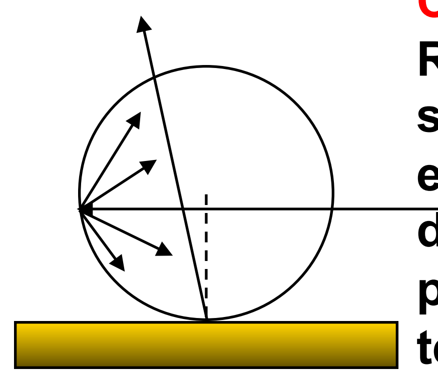
0°:45°

ASTM E1164: **Obtaining Spectrometric Data for Object-Color Evaluation**

Hemispherical



~0°:d



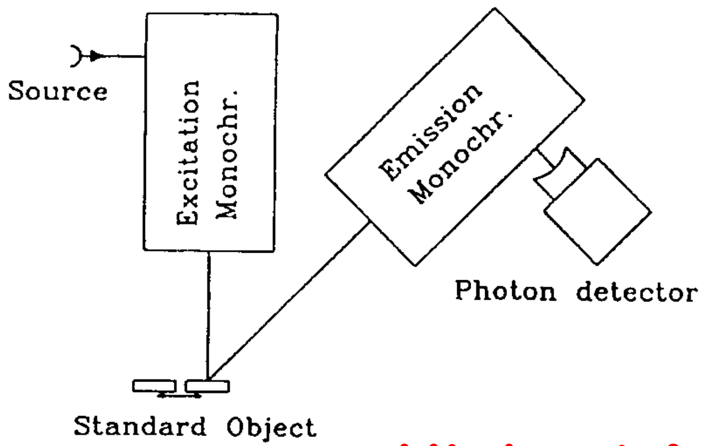
d:~0°

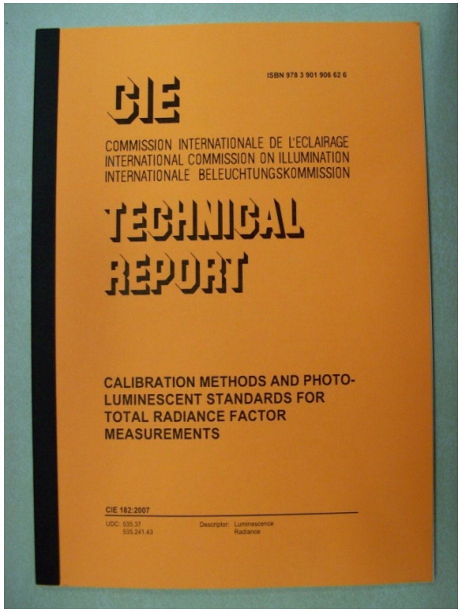
Practical Colorimetry: **Recommended for samples exhibiting directionality, e.g. paper (ISO 2469), textiles (AATCC)**

Reference Documents

Measurement of Fluorescent Colour: CIE Standards

CIE 182:2007



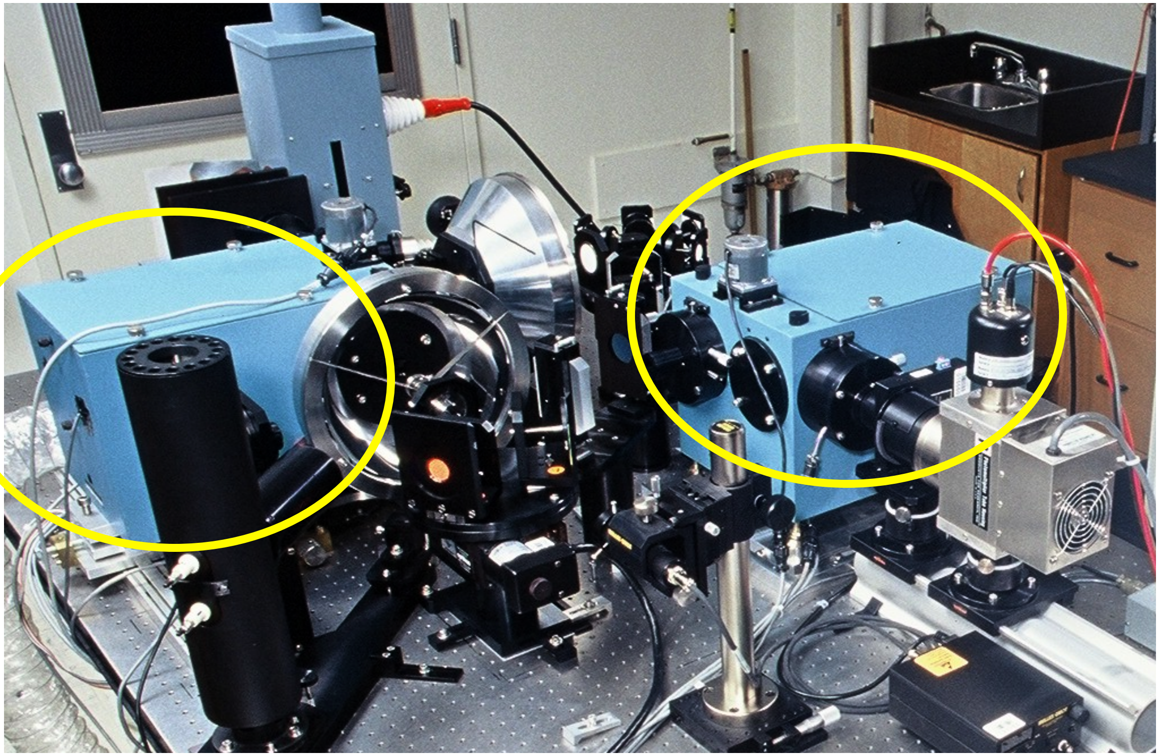


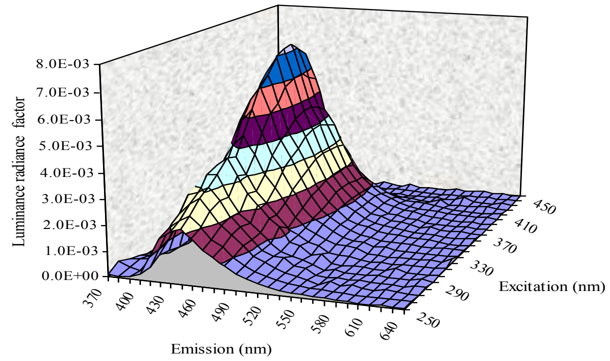
Calibration Methods and Photoluminescent Standards for Total Radiance Factor Measurements

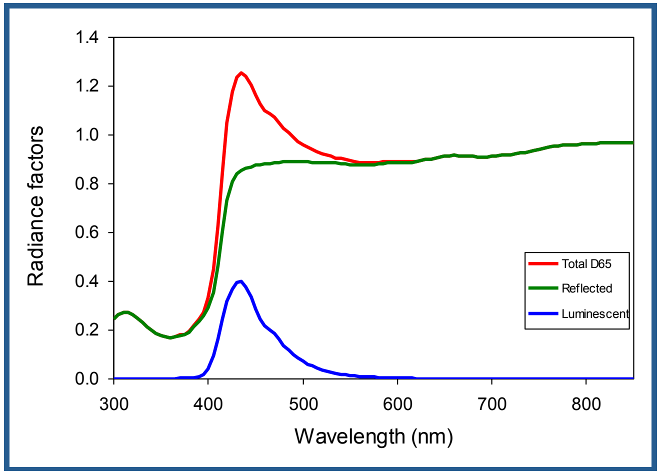
Highest Accuracy:

- Two-monochromator method
- 45:0 or 0:45 geometry is preferable

NRC Reference Spectrofluorimeter







- Based on two-monochromator method
- **Measurement geometry: 45°a/0°**

  J. Zwinkels et al., *Applied Optics*, **36**, 892-902 (1997)

Traceability of Fluorescence

Linking Fluorescence Measurements to SI Radiometric Scales – Physical Transfer Standards (PTS)

All PTS: Calibrated for 45:0 Geometry

↓

Fluorescent samples : Traceability to 45:0 geometry

Cryogenic Radiometer

Spectral responsivity [A/W]

→ **SI: CCPR Key Comparisons**

Physical Transfer Standards

Detector, Source and Reflector Standards

→ **Instrument Calibration**

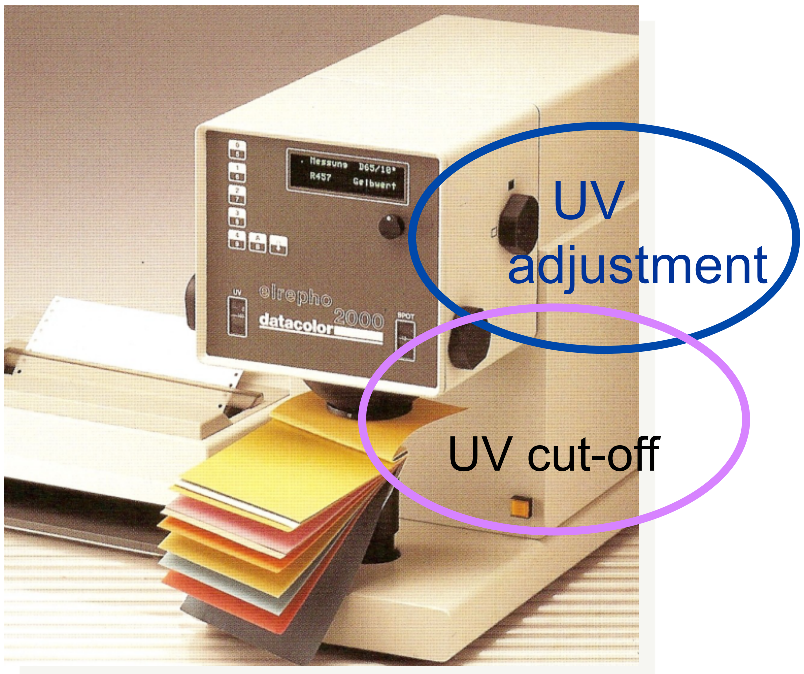
Reference Spectrofluorimeter

Spectral characteristics

Photometric scale

→ **Fluorescent sample calibration: Color quantities, quantum yields**

Practical Fluorescence Colorimetry One monochromator Poly mode



Sphere geometry
d:0 (paper applications)
de:8 or di:8 (textile applications)

Instrument calibration with calibrated transfer standards:

Photometric scale: non-fluorescent
Colorimetrric scale: fluorescent

1 point - UV adjustment →
One colorimetric quantity
e.g. D65 whiteness

Traceability requirements:

Standard is similar to test sample →
- Same excitation/emission
- Same measurement geometry

Effect of Measurement Geometry

Bispectral (45:0 or 0:45)

- CIE Reference geometry for fluorescence measurements
- Gives **spectral radiance factor**
- Source SPD does not change with sample emission
- Design of reference instruments for calibrating fluorescent standards

Sphere (d:0, de:8, di:8)

- CIE recommended geometries for general colorimetry
- Gives **spectral reflectance factor**
- Source SPD is altered by sample emission – ***Spectral sphere error***
- Design of commercial instruments commonly used for measuring fluorescent samples: paper, textiles

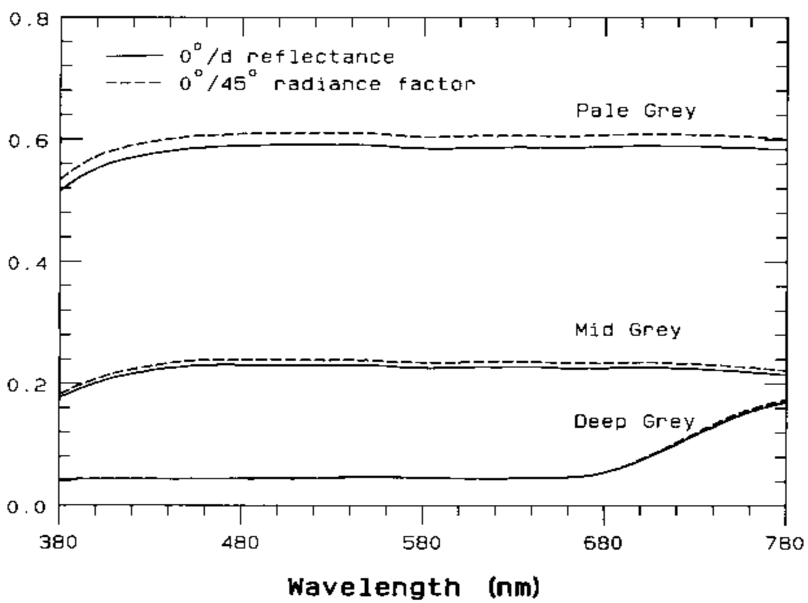
Traceability Issue: transfer of scale
Need for Geometric Correction

Geometric Correction

General reflecting material

- Sample dependent
- Wavelength independent

BCRA grey tiles



R(de:0) = α R(45:0)

α = geometric correction factor

Magnitude of Correction:

- White reflectance standards: α = 0.985
- BCRA grey tiles: α = 0.965
- Non-fluorescent white paper: α = 0.985

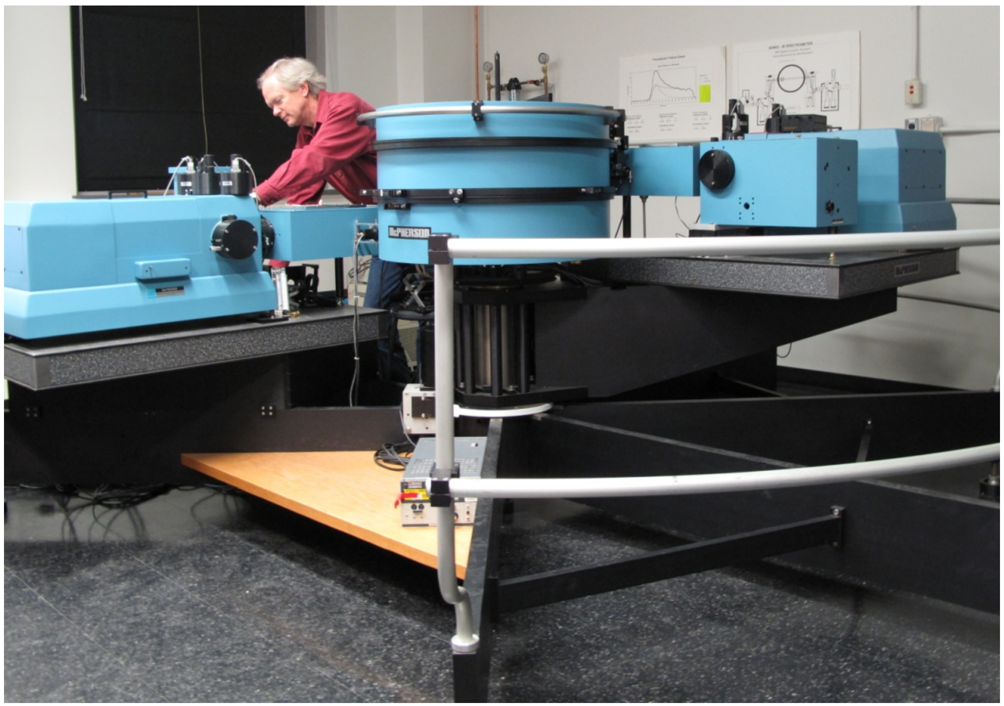
Fluorescent reflecting material

*Q. Do **reflected** and **fluorescent** components have the same correction?*

NRC Goniospectrofluorimeter (GSF)

Gonio – variable angles of incidence and detection

Donated to NRC in 2009 by 3M Co.
Complements the NRC Reference Spectrofluorimeter

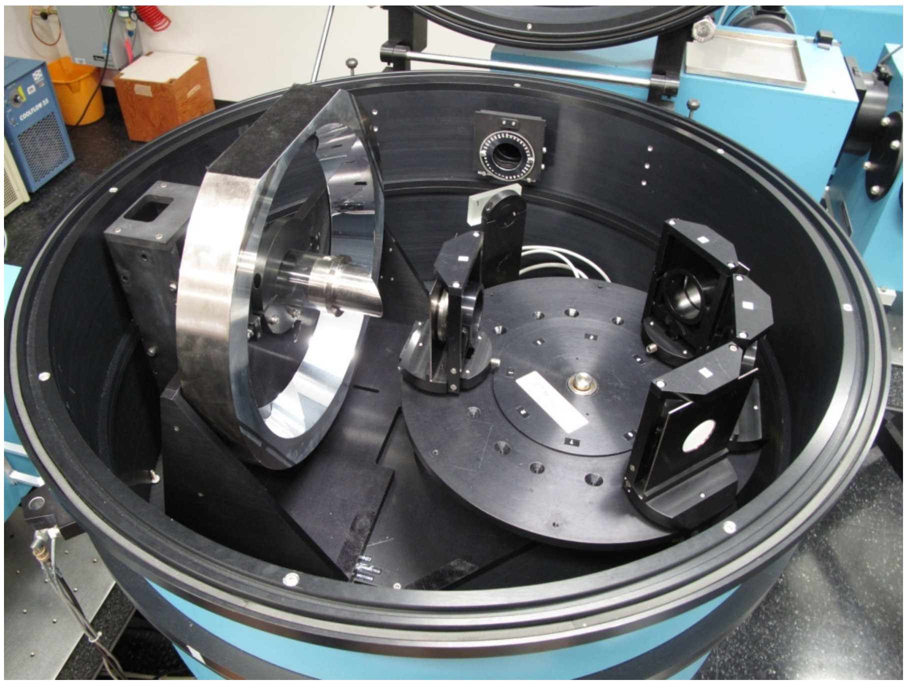


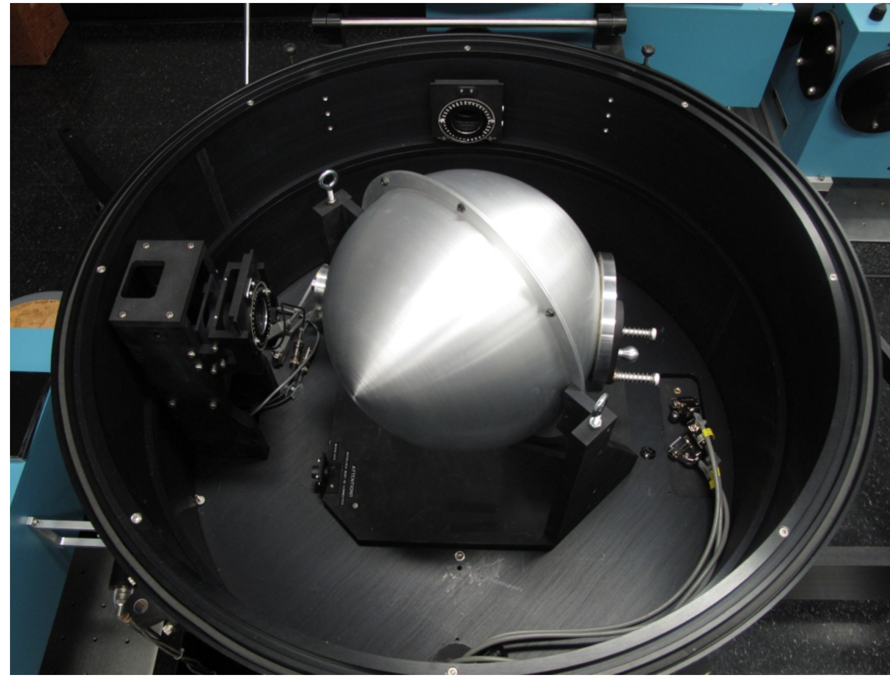
Gonio- spectral fluorescence:

Spectral range: 300- 850 nm
Spectral bandpass: 5 nm
Incidence: 0° to 90°
Viewing: 22° to 180°
Sample beam: 25 mm diam.

Several Measurement Geometries

Bidirectional reflectance/
fluorescence (45a:0)





Hemispherical reflectance/
fluorescence (sphere)

Extension to Other Geometries: Gonio- and Sphere

Motivation:

Research Optical Properties of Materials

- Gonio-characteristics of fluorescent white standards

New Calibration Services

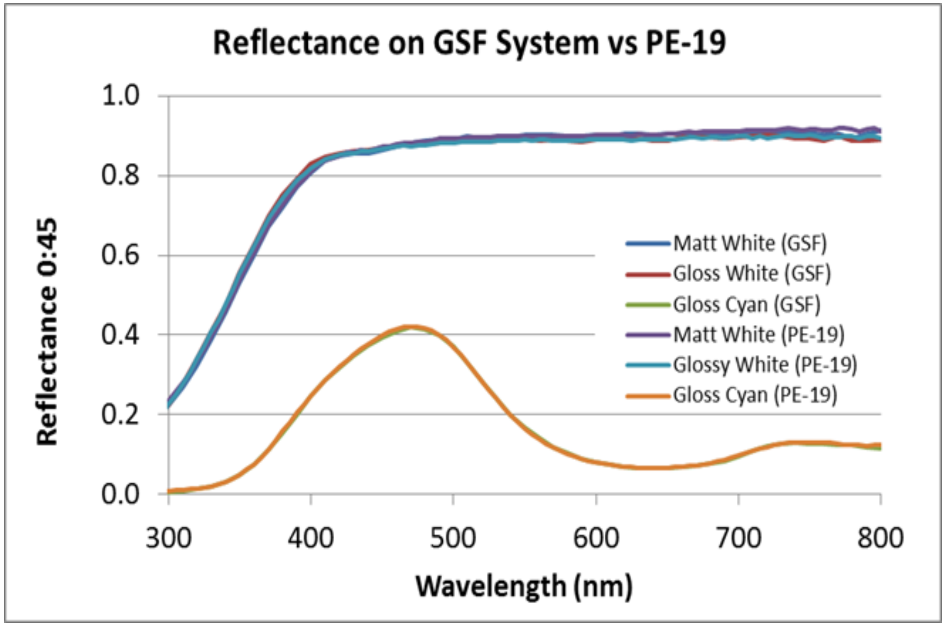
- Gonio-apparent fluorescent materials(security, decorative materials)

Improved Traceability

- Study geometric dependence: primary c.f. transfer calibrations
  - **Reference measurements: bidirectional geometry (45:0) c.f.**
  - **Commercial instruments & Standard Test Methods (ISO, ASTM, AATCC) : sphere geometry (d:0, de:8, di:8).**

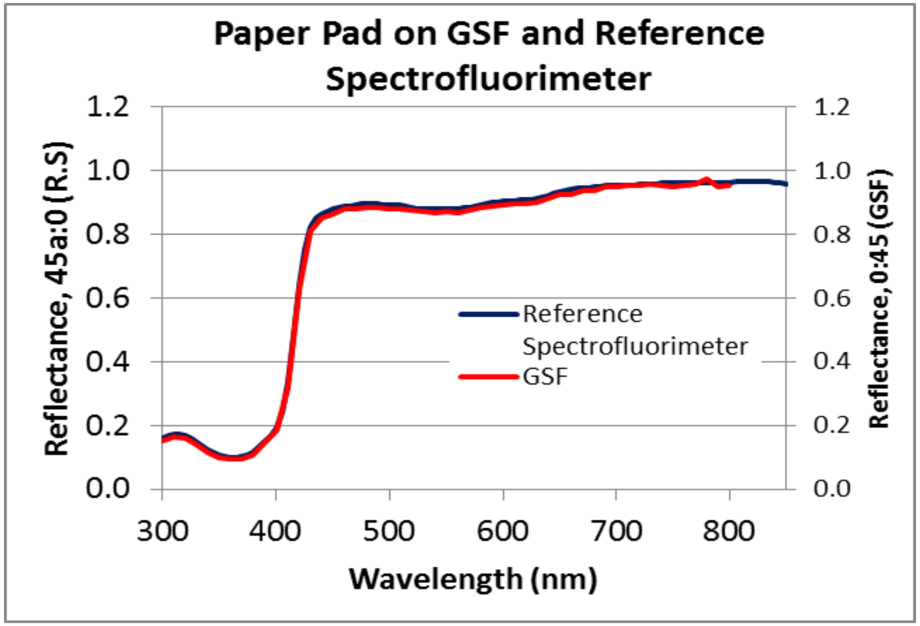
Validation of GSF– Reflected component (45:0 geometry)

Non-fluorescent tiles



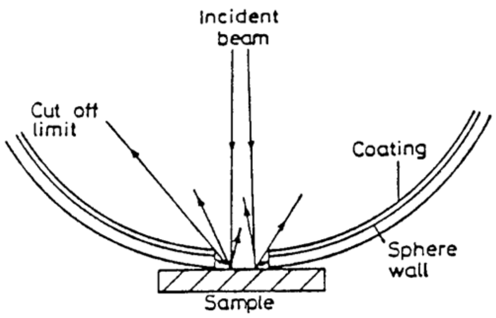
c.f. PE-19 , 0:45a geometry

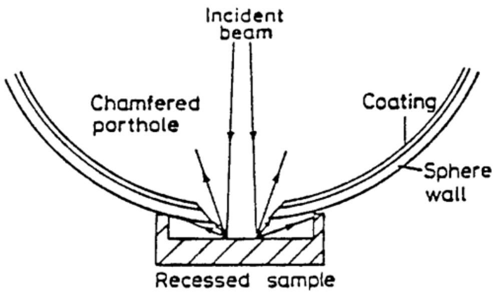
Fluorescent paper pad

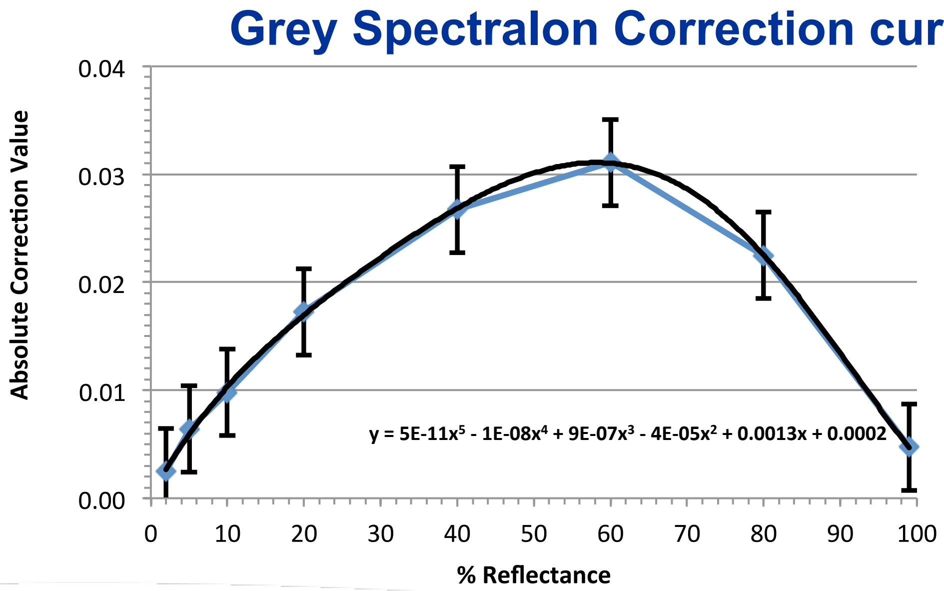


c.f. NRC Reference spectrofluorimeter, 45a:0 geometry

Sphere Errors – Sample recess

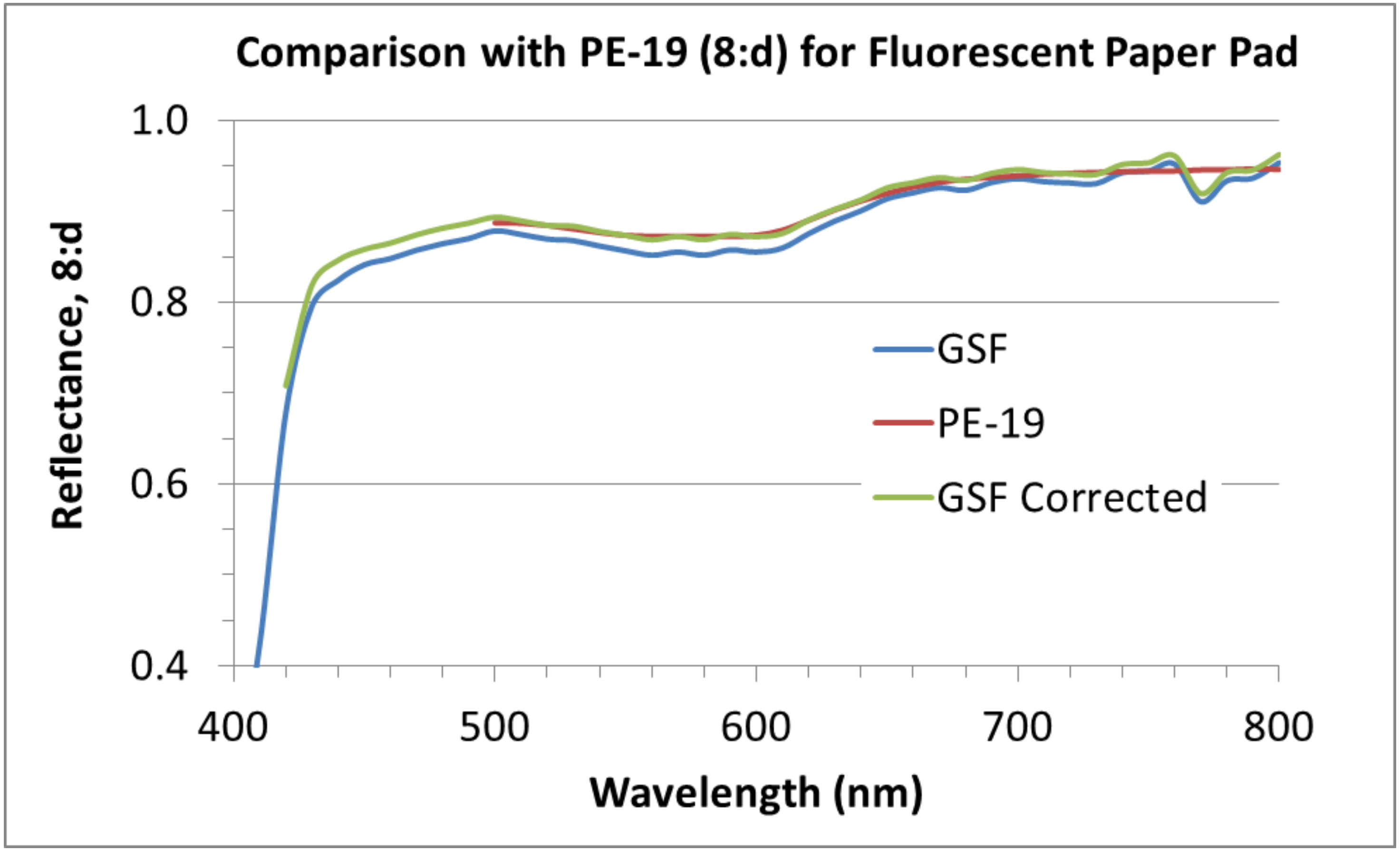






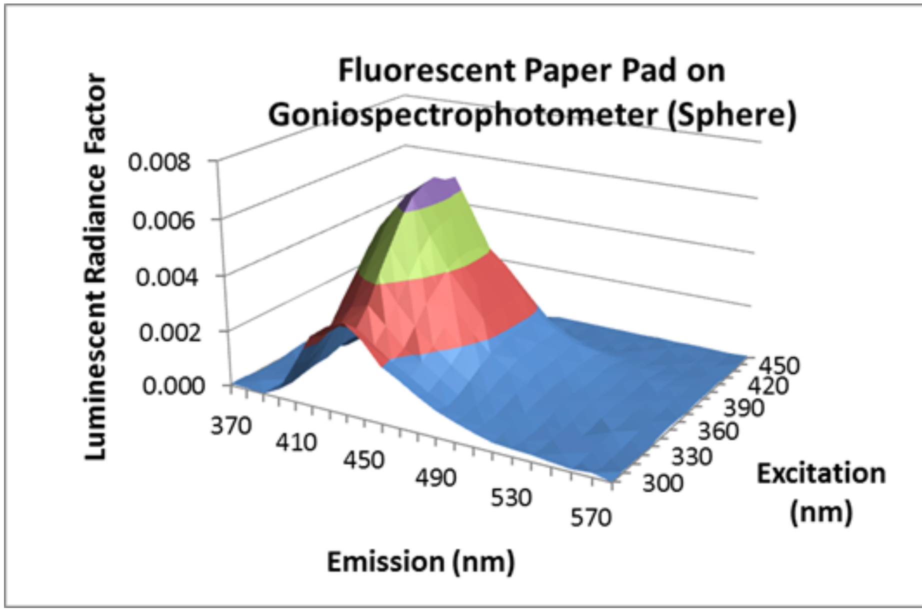
PTFE sphere accessory (! ~6 mm thick)

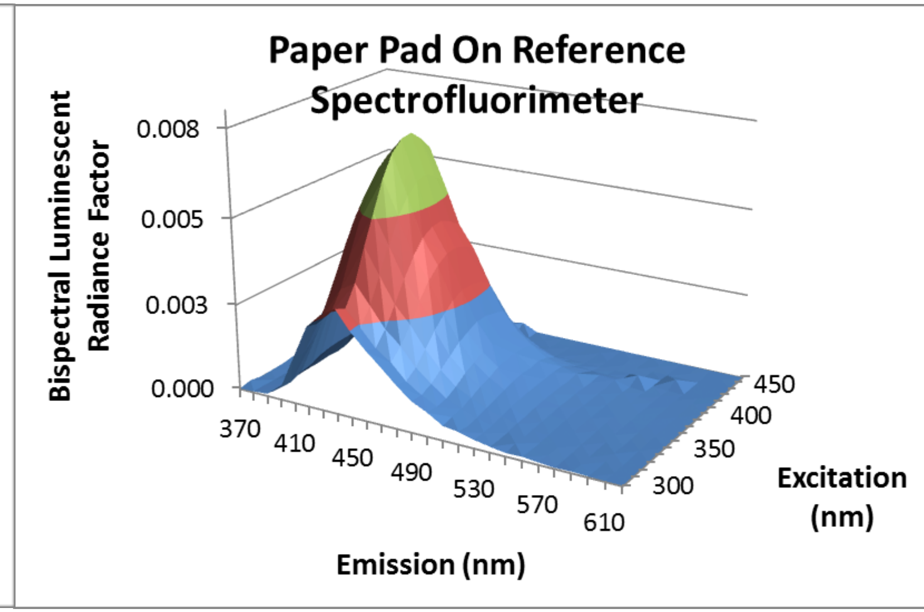
Validation of GSF – Reflected component (8:di geometry)



Bispectral Fluorescence Results
Sphere vs 45:0 geometry - Preliminary

Fluorescent White Paper Pad



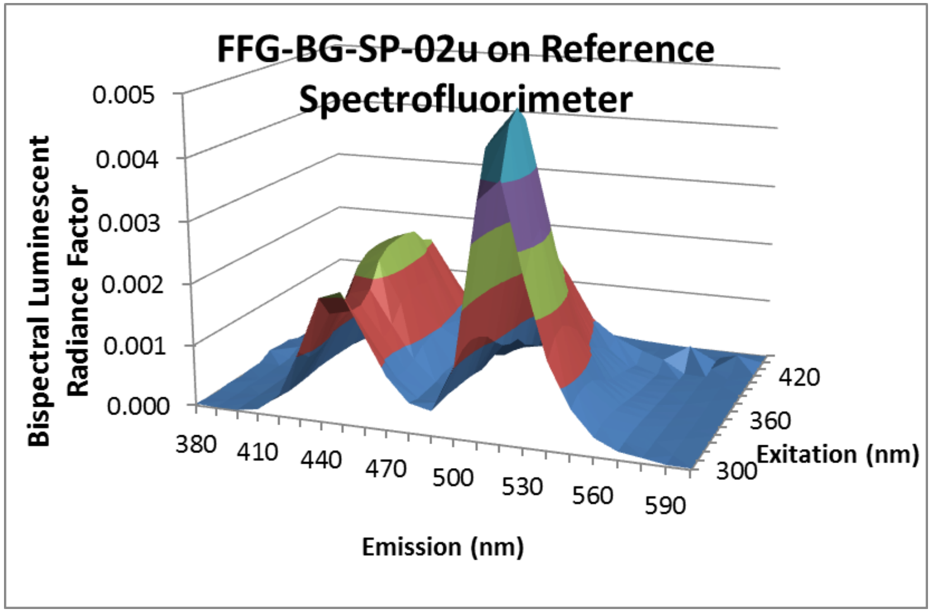


Sphere

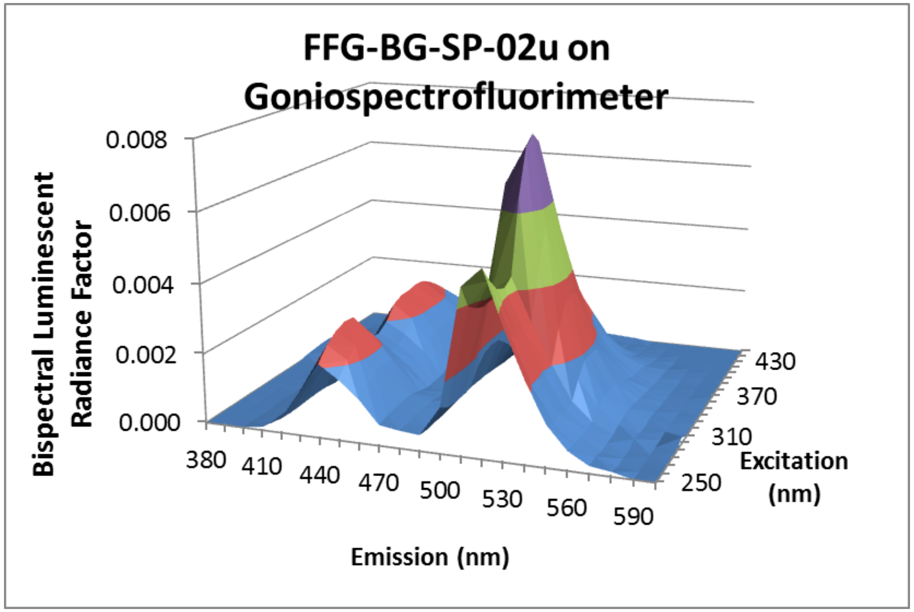
45a:0

Bispectral Fluorescence Results 45:0 vs Sphere geometry - Preliminary

Fluorescent Blue-Green Spectralon



45a:0



Sphere

Conclusions

- Traceability issues in fluorescence colorimetry
  - CIE reference (45:0) vs. practical (sphere) geometries
- Status of NRC Goniospectrofluorimeter validation
  - 45:0 measurements
  - sphere measurements
- Study of geometric dependence of fluorescence
  - Preliminary results
- Next steps to improve traceability:
  - Further characterize / correct sphere measurements
    - Single-beam substitution error
    - Spectral sphere error
  - Complete validation/ uncertainty budget

Thank you

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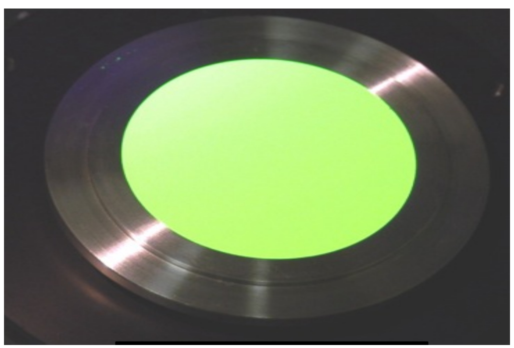
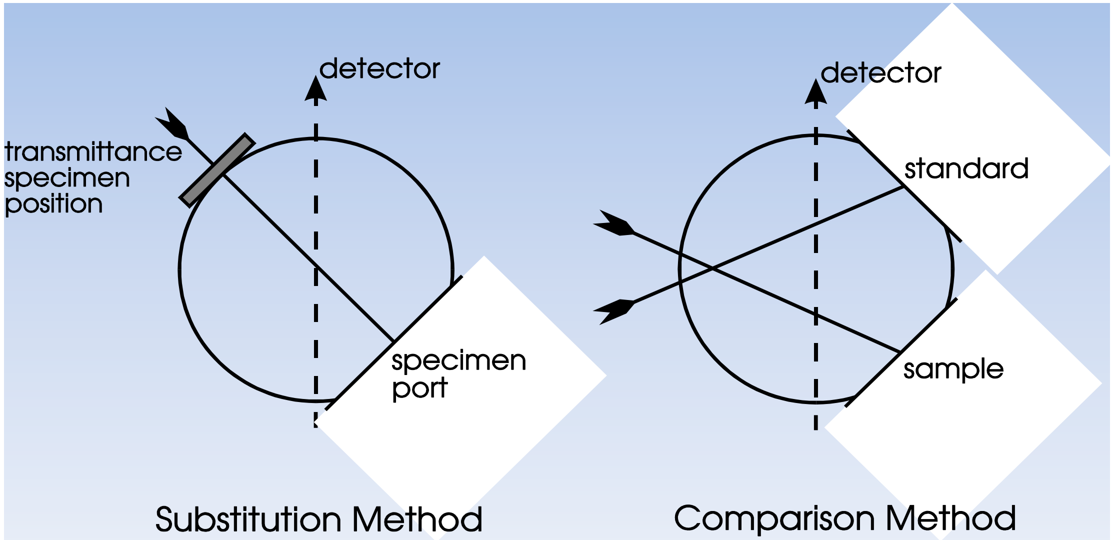


NRC Fluorescence Measurements

Table 2. Uncertainty Budget for the **Total** Radiance Factors of Fluorescent Reflecting Materials Measured on NRC Reference Spectrofluorimeter in the Visible Range

Uncertainty Component	**Type**	**Relative Standard Uncertainty**	**Uncertainty Contribution**	**Typical** (λ = 450 nm; D65 illuminant)
Wavelength Scale[1]	B	$u(\lambda)$ = 0.1 nm	$u(\lambda)\,(\partial\beta_T/\partial\lambda)$	0.0008
Bandpass[2]	B	0.03% at peak	f$(\partial^2\beta_T/\partial^2\lambda)$	Negligible
Linearity and Photometric Accuracy[3]	B	<0.2%	Abs(0.002 β_T (1- β_T))	0.00054
Polarization[4]	B			Negligible
Stray Light[5]	B	<0.0006	0.0006/ β_T	0.0005
Temperature (ΔT = 1.0 °C)[6]	B	0.018 nm/°C	0.02 $u(\lambda)\,(\partial\beta_T/\partial\lambda)$	0.00002
Long Term System Stability[7]	B	<0.2% per year	$(\beta_{T,MAX} - \beta_{T,MIN})/\sqrt{12}$	0.00005
45°:0° Reflectance Scale[8]	B	$u(\beta_R) = 0.00265$	0.0023 β_R	0.0020
45°:0° Luminescent Scale[9]	B	$u(\beta_L) = 0.005$	0.005 β_L	0.00167
Luminescent Measurement Reproducibility[10]	A	$u_S(\beta_L)$	$(\beta_{L,MAX} - \beta_{L,MIN})/\sqrt{12}$	0.00085
Reflectance Measurement Reproducibility[11]	A	$u_S(\beta_R)$	$(\beta_{R,MAX} - \beta_{R,MIN})/\sqrt{12}$	0.0017
			Combined standard uncertainty	0.0034
			Coverage Factor, *k*	2
			Expanded Uncertainty, (*k* = 2)	**0.0068**

Substitution vs Comparison



Substitution (single-beam sphere) - simpler design and improved sensitivity; subject to **photometric scale error dependent on difference in reflectivities of sample and standard**

Comparison (double-beam sphere) - comparison standard remains fixed in position; dynamic compensation prevents changes in sphere efficiency for measurements of sample and reflectance standard at specimen port

Single-beam Substitution Error

- *Change in the sphere efficiency (spectral transmittance) when sample or standard are present*
- - both the reflected and emitted power from the sample change the average sphere wall reflectance.
- In a double-beam instrument, this error is corrected for measurement of **non-fluorescent samples** by use of use of “dummy port” – ratio sample or standard signal to fixed (non-fluorescent) comparison sample at dummy port.
- For **NRC sphere-based fluorescence measurements** **, to correct for this error:**
  - Need to measure and correct for change in sphere efficiency due to reflected and emitted components, separately.

Geometric Correction

Fluorescent reflecting material

*Do **reflected** and **fluorescent** components have the same correction?*

ISO TC6 (Paper, pulps and board)

Initially: correction was applied to the **total radiance factor data**, i.e. assumed reflected and fluorescent components – SAME

Current practice: correction is applied to **reflected component only**

Other issues that need to be resolved:

Who should carry out this geometric correction?
- the standardizing lab or the secondary lab?

- **ISO TC6:** the secondary labs (ALs) make necessary correction