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Extension of NRC fluorescence measurement capabilities

Zwinkels, Joanne; Noel, Mario; Neil, Bill

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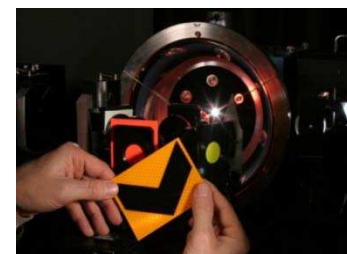


CORM 2012, Session I, 30 May 2012
NRC Sussex, Ottawa, Canada

Extension of NRC Fluorescence Measurement Capabilities

Joanne Zwinkels, Mario Noel and Bill Neil

NRC Measurement Science and Standards



National Research
Council Canada

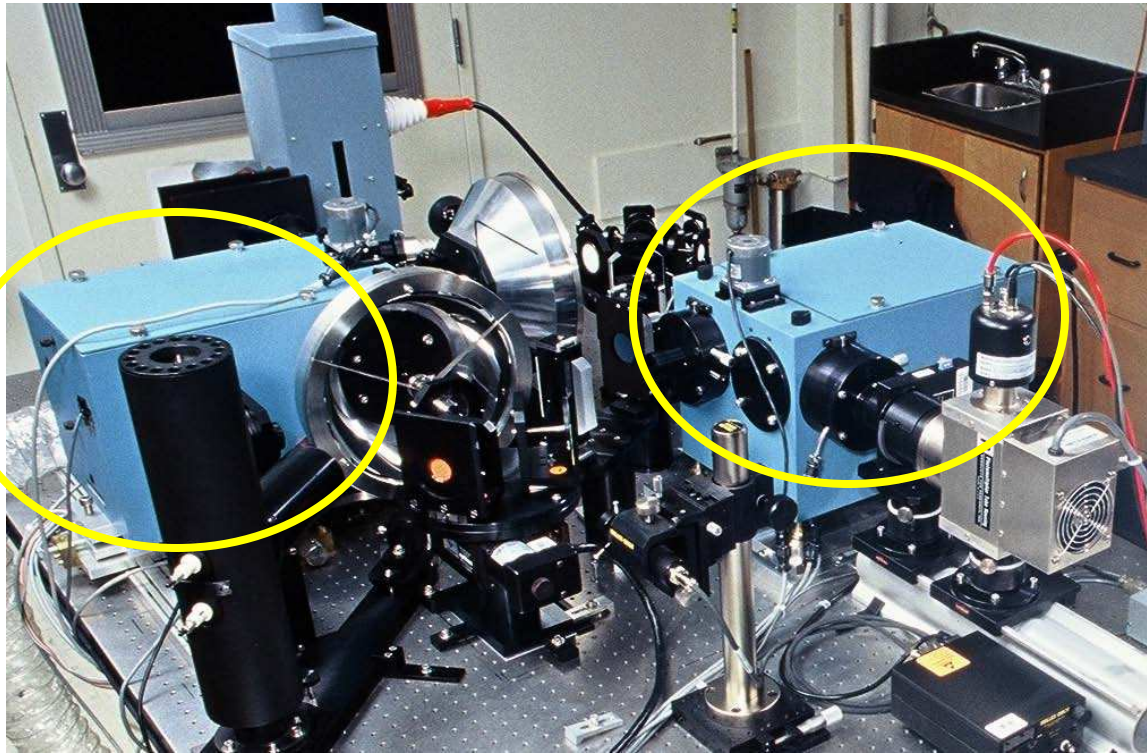
Conseil national
de recherches Canada

Canada

Outline

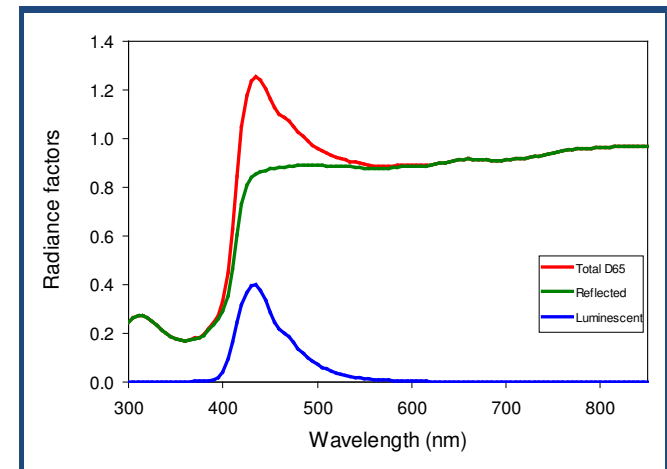
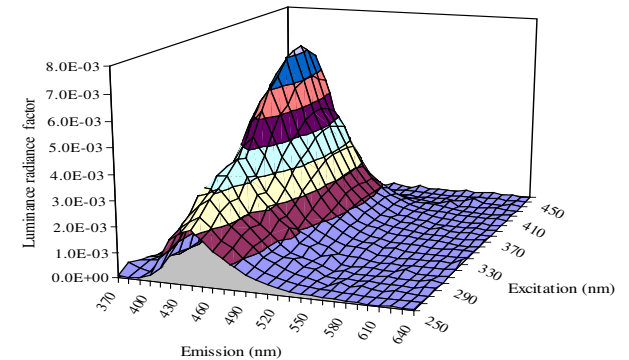
- Background of NRC Fluorescence Project
 - Instrumentation & services: surface fluorescence
- Extension to Volume Fluorescence
 - Results of international comparison
- Extension to NIR Fluorescence
 - Impact on use of colour standard tiles
- Extension to Other Measurement Geometries
 - 3M Goniospectrofluorimeter Facility
 - Preliminary characterization results

NRC Reference Spectrofluorimeter



- Based on two-monochromator method
- Measurement geometry: $45^\circ\text{a}/0^\circ$

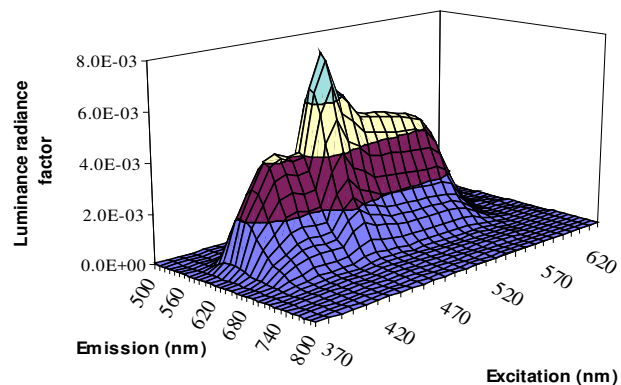
J. Zwinkels et al., *Applied Optics*, **36**, 892-902 (1997)



Why Calibrate?

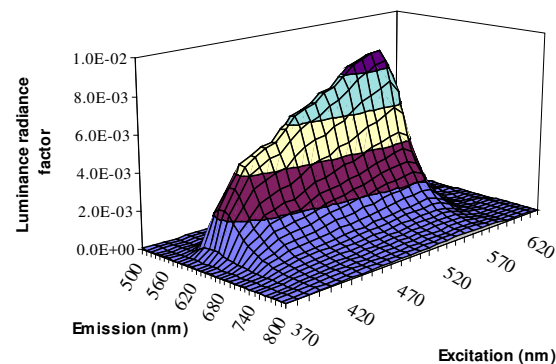
Raw “Measured”

Raw Bispectral Luminescent Radiance Factor

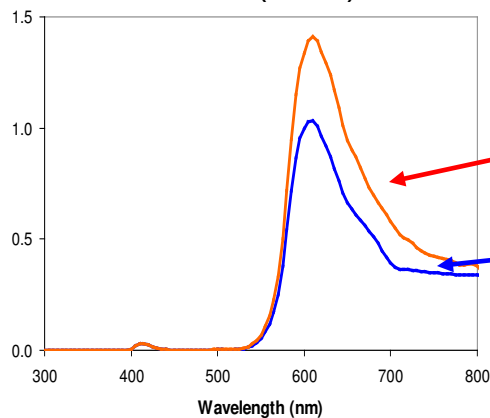


After Calibration

Normalized Bispectral Luminescent Radiance Factor



Total (D65)



True result
“after calibration”

Erroneous result
“raw” data

Surface Fluorescence

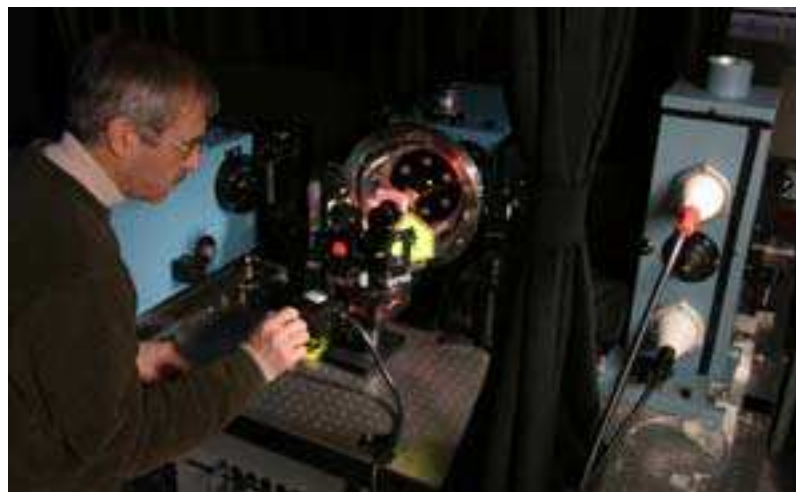
NRC Calibration Services

Solid Samples: Paper, textile, paint, plastics, pressed powders

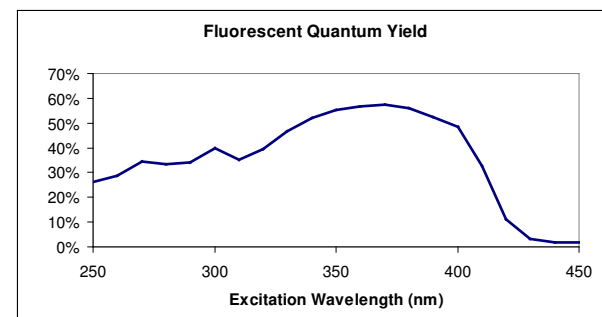
Total Spectral Radiance Factors

$$\beta_T(45^\circ a/0^\circ); \quad \beta_T = \beta_R + \beta_F$$

- 300 – 850 nm, 5 nm bandpass
- Selected illuminants (CIE D65, C,A, D50, custom)
- In accordance with ASTM and CIE **colorimetry** standards



Spectral Quantum Yields



Extension to Volume Fluorescence

Background:

- Increasing use of fluorescence techniques as a quantitative analytical tool
- Increase in biological and medical applications of fluorescence, e.g. probes and labels
- Increasing diversity of fluorescence instrumentation
- Fluorescence measurements are very dependent on instrument-specific effects (wavelength, polarization, aging)



Standardization is critical - comparable fluorescence data

Extension to Volume Fluorescence

**NRC – invited to participate in an International Comparison of
Correction of Emission Spectra**

Specifications for Intercomparison:

SAMPLES: fluorescent dyes

- Transparent
- Side-viewing
- 0°/90° geometry
- High resolution (1 or 2 nm)
- Low concentration (weak fluorescence)
- **LIQUIDS**

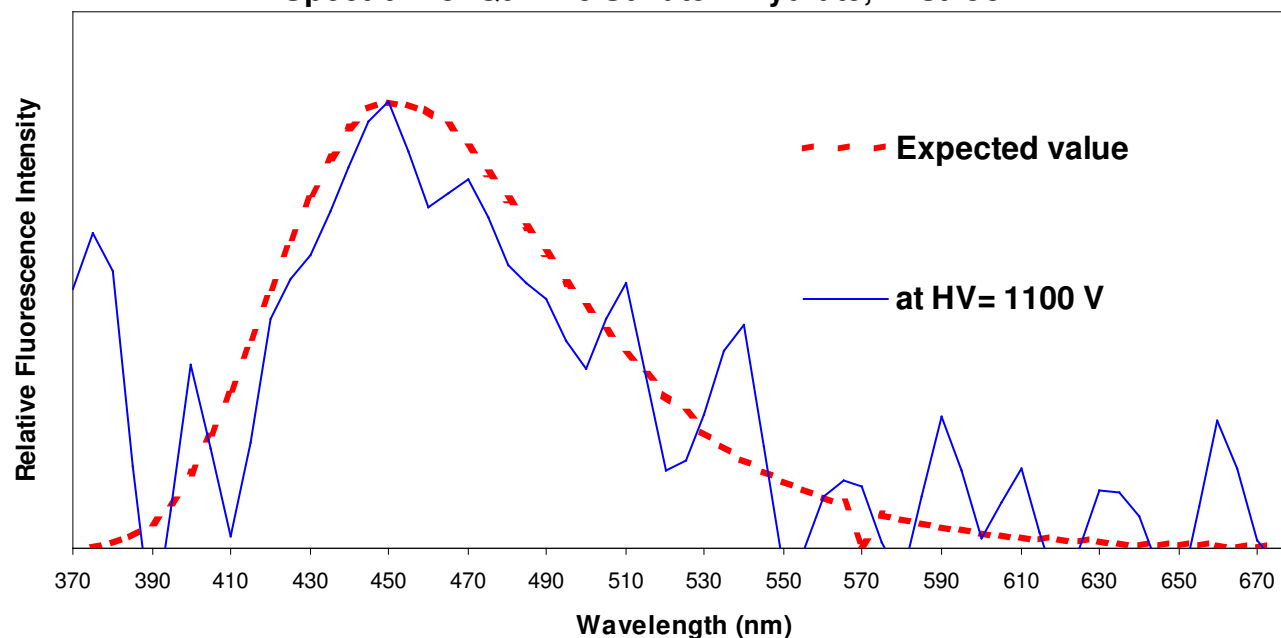
Specifications of NRC Spectrofluorimeter:

IDEAL: fluorescent surface colours

- Opaque
- Front-surface viewing
- 45°/0° geometry
- Medium resolution (5 nm)
- Moderate to strong fluorescence
- **SOLIDS**

Preliminary NRC Results

Spectrum of Quinine Sulfate Dihydrate, First look !



$S/N \sim 5:1$

=> Need to
Increase **S**
and
Decrease **N**

Increase S:

- Optimize sample presentation
- Optimize system throughput

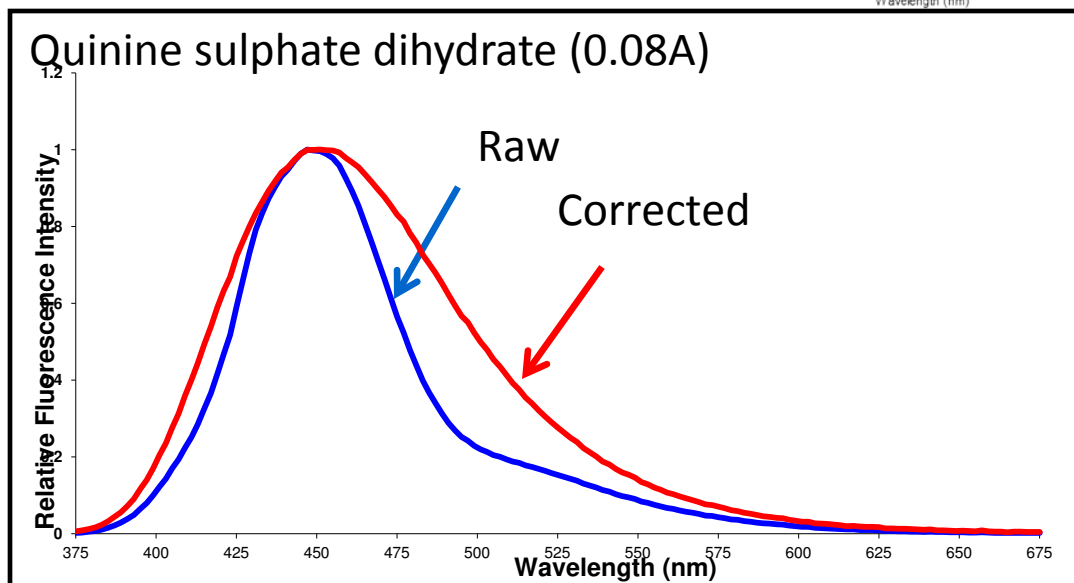
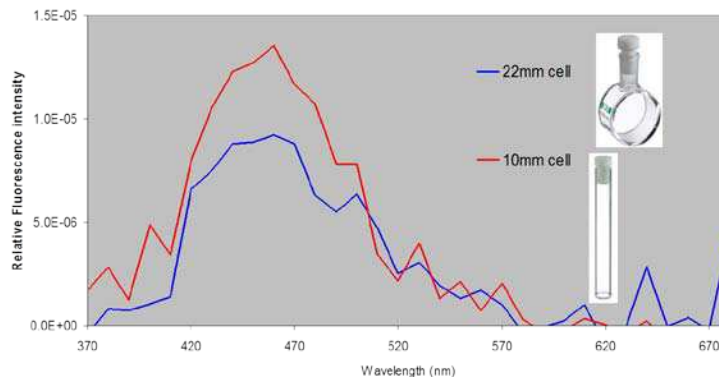
Decrease N:

- Reduce noise sources

Extension to Volume Fluorescence

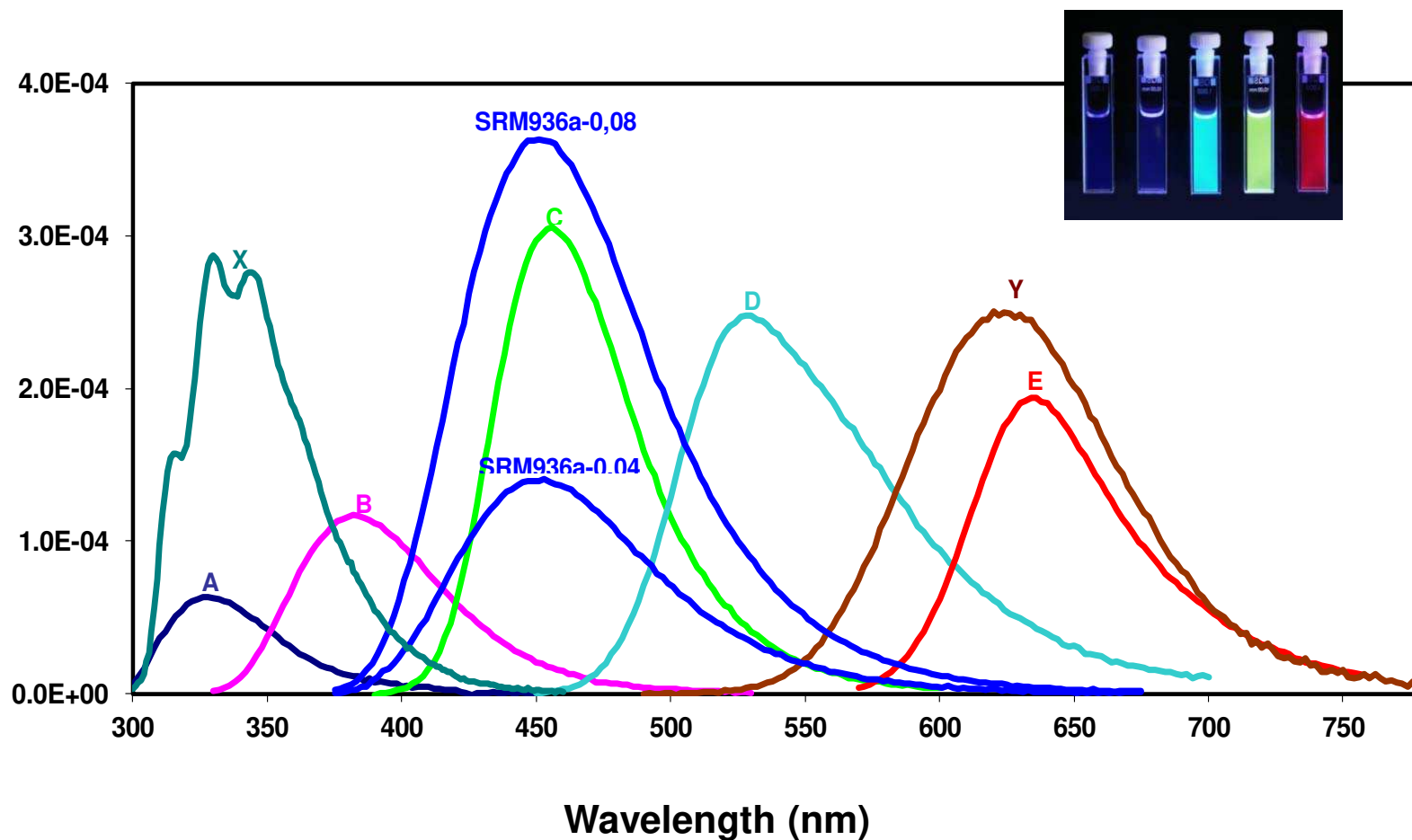
Re-optimization of instrument parameters

- No ground loops
- No cooler switching noise
- Choice of cuvette
- Cuvette positioning
- PMT high voltage



S/N ~ 100:1
(20x
improvement)

NRC Final Comparison Results



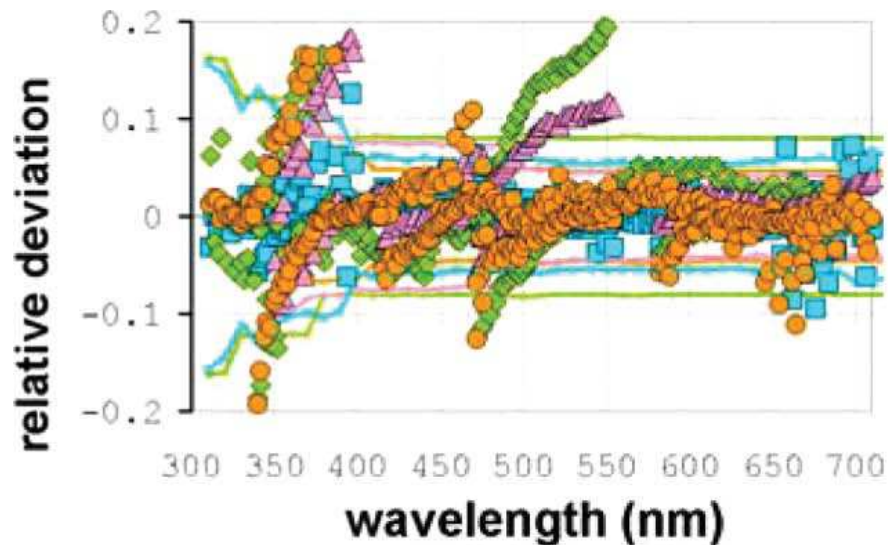
Uncertainty Analysis – Volume Fluorescence Measurements



Uncertainty Component	Type	Standard Uncertainty (k=1)	Relative Uncertainty
Measurement repeatability	A	1.0%	1.0%
Wavelength	B	0.10 nm	0.2%
Detector linearity	B	<0.20%	<0.20%
Radiometric calibration of emission unit			
Spectral irradiance standard	B	3.0 – 0.5%	3.0 – 0.5%
Spectral radiance factor standard	B	0.2%	0.2%
Transfer of relative spectral emission calibration	B	0.4%	0.4%
Total expanded (k=2) uncertainty			6.4 – 1.2%



Spectral Emission Correction Comparison Results



Participants:

- NIST
- BAM
- PTB
- NRC

State-of-the-art
comparability of
corrected
emission spectra
~4.2%

U. Resch-Genger et al. Anal. Chem., 84, 3889-3898 (2012)

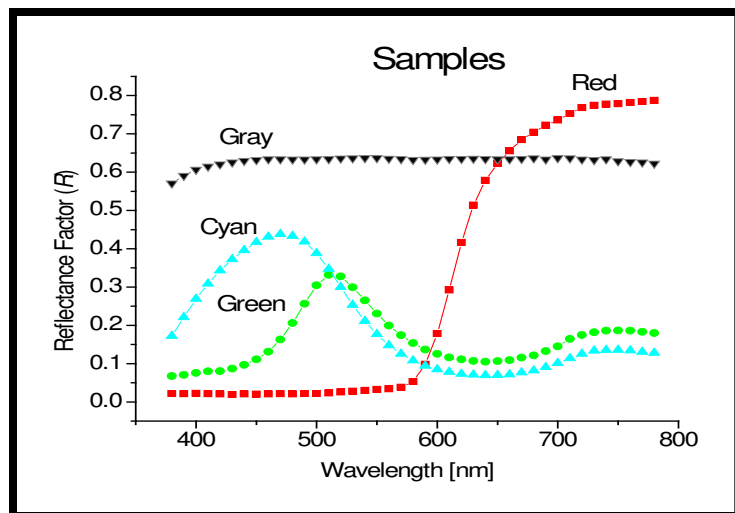
Fluorescence Research

Colour standards:

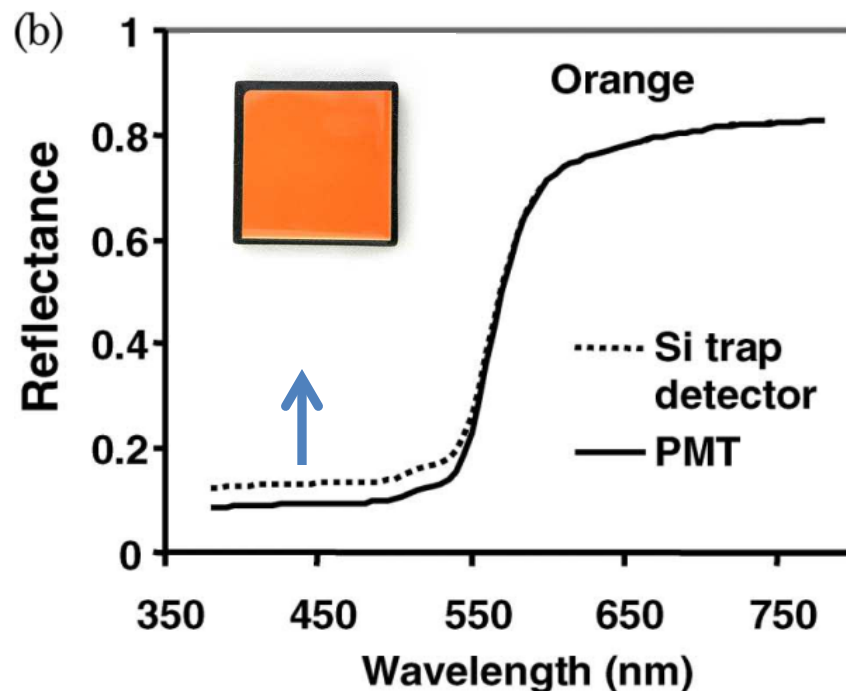
Requirement: reflectance is independent of mode of measurement



CCS Colour Tiles



Monoch. Illumination/
polych. detection

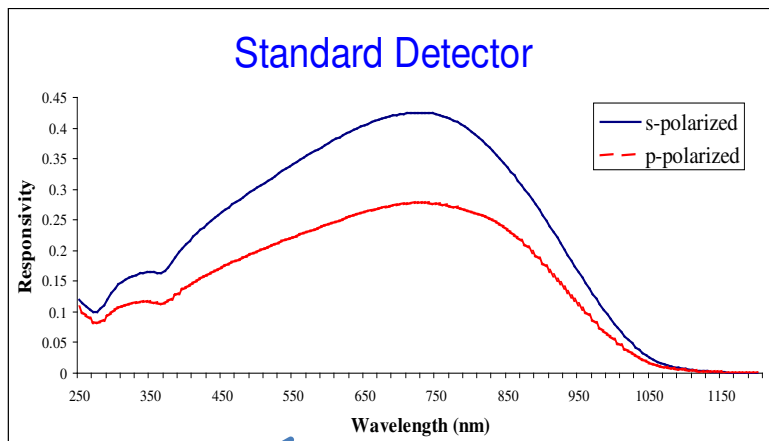


Koo, A. et. al, *Appl. Opt.*, 49, 2375-2381(2010)

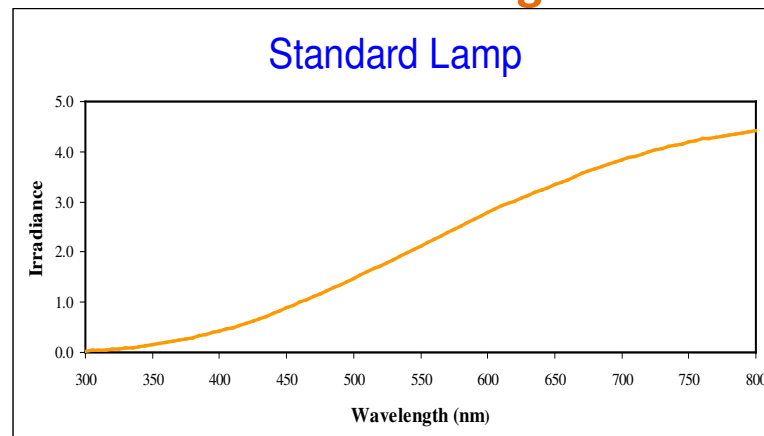
Nadal, M., Miller, C., and Zarobila, C., *Color Res. Appl.*, (2010)

Traceability of NRC Fluorescence Measurements

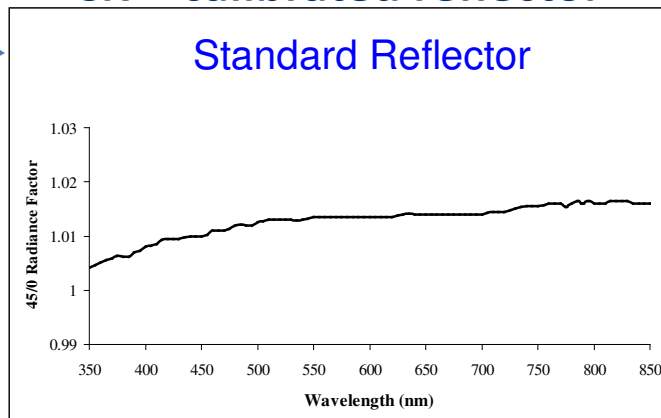
CD = calibrated detector



CS = calibrated light source



CR = calibrated reflector



CD:

1. Calibrate monitor detector

CD-CR:

2. Calibrate excitation unit

CS-CR:

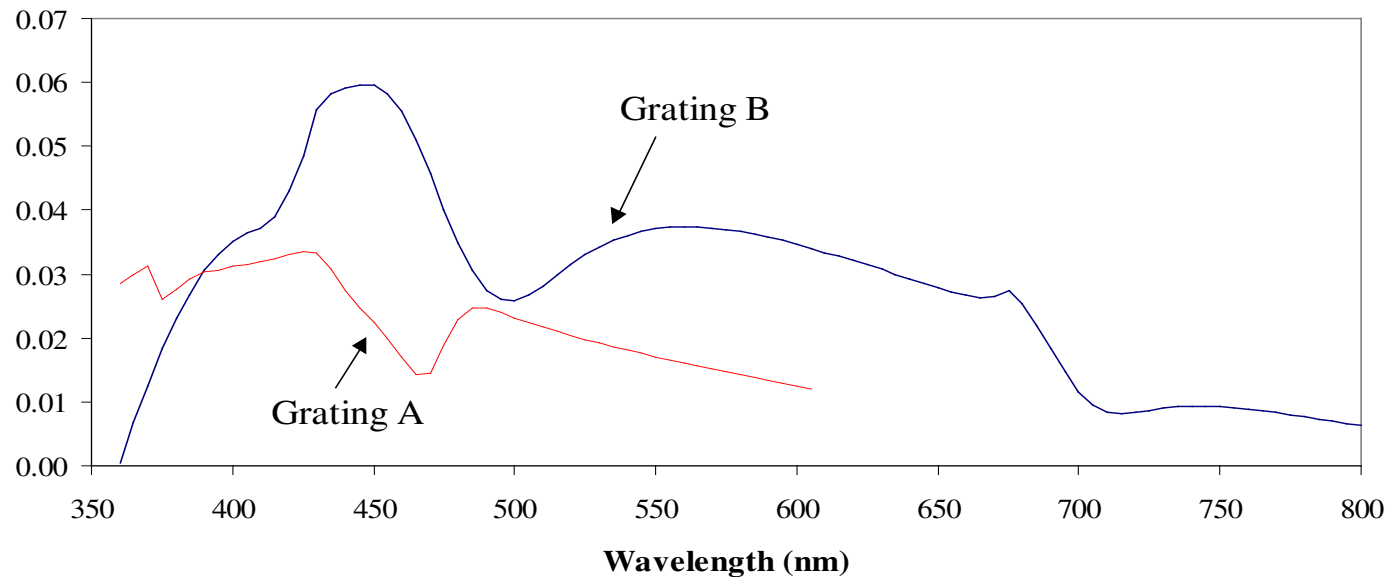
3. Calibrate emission unit

Spectral Emission Calibration

Three Methods:

- Physical Transfer Standards: **CS-CR**
- Physical Transfer Standards: **CD-CR**
- Certified Reference Material: **RM**

Existing Calibrated Spectral Range: 300 nm to 800 nm (**CS-CR** method)

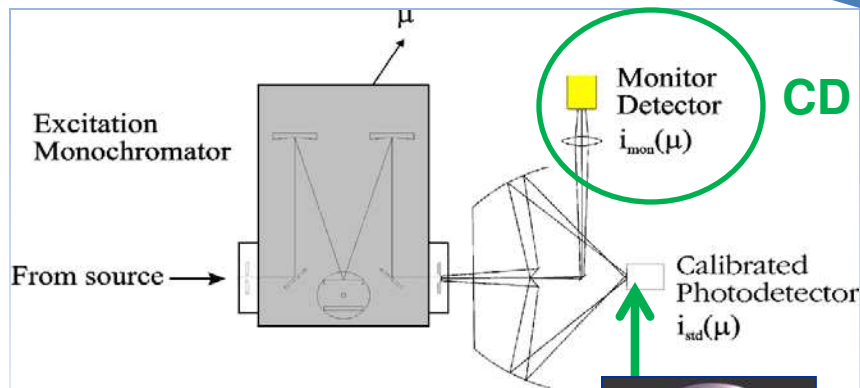
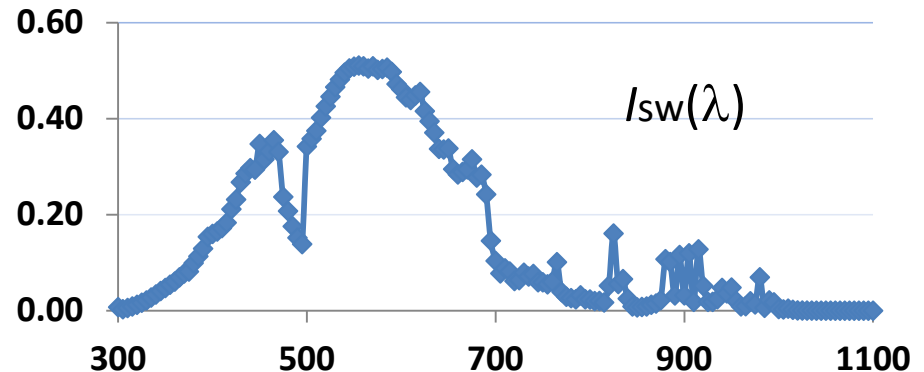


Extension to NIR:

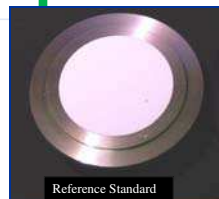
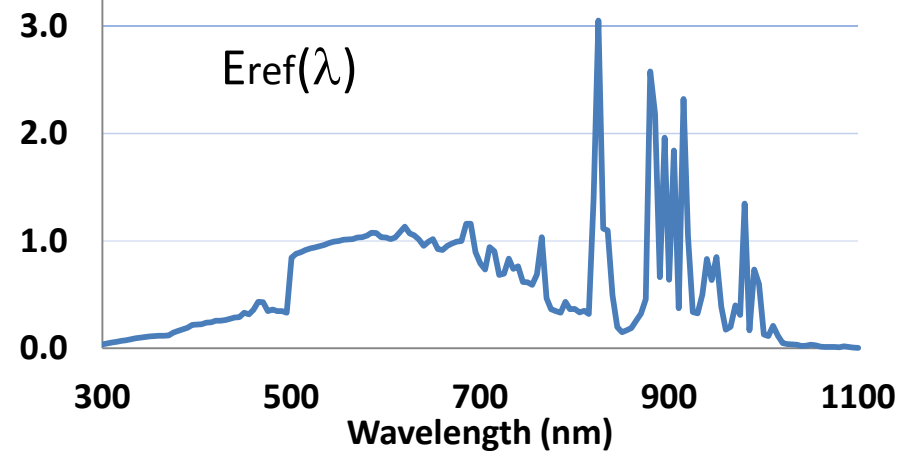
CD-CR Method

Emission Unit Spectral
Responsivity, $R_{sys}(\lambda)$

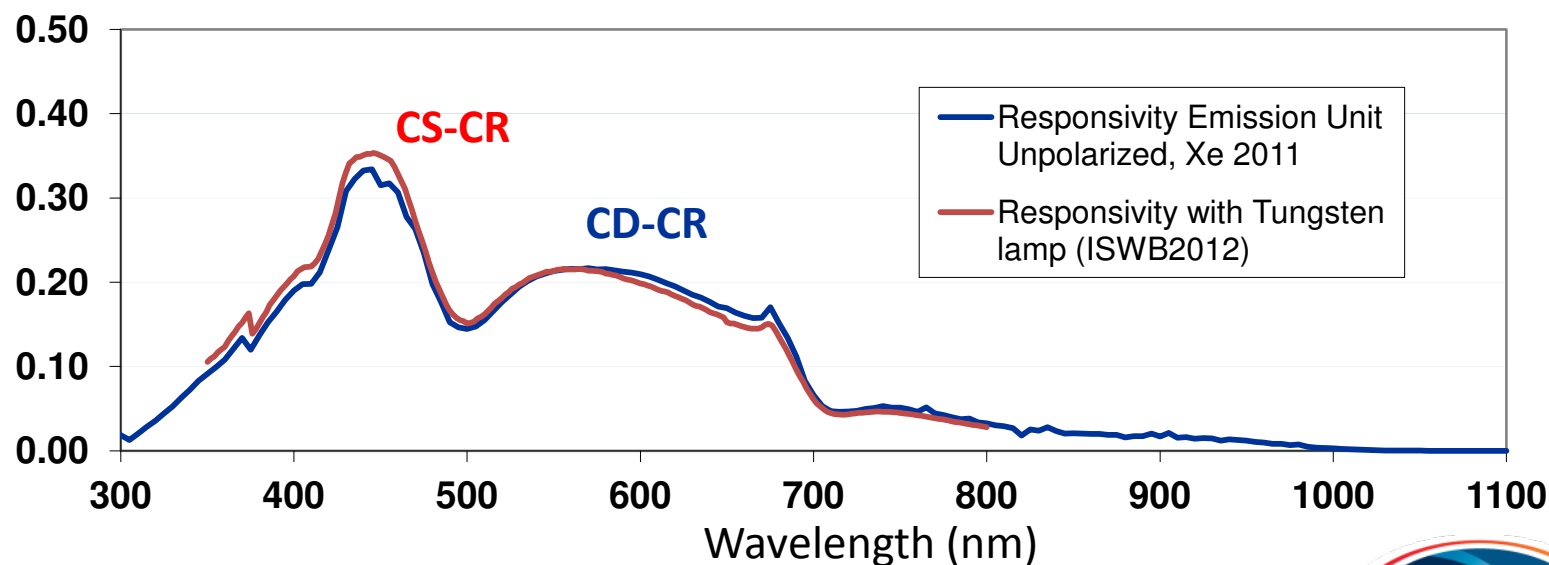
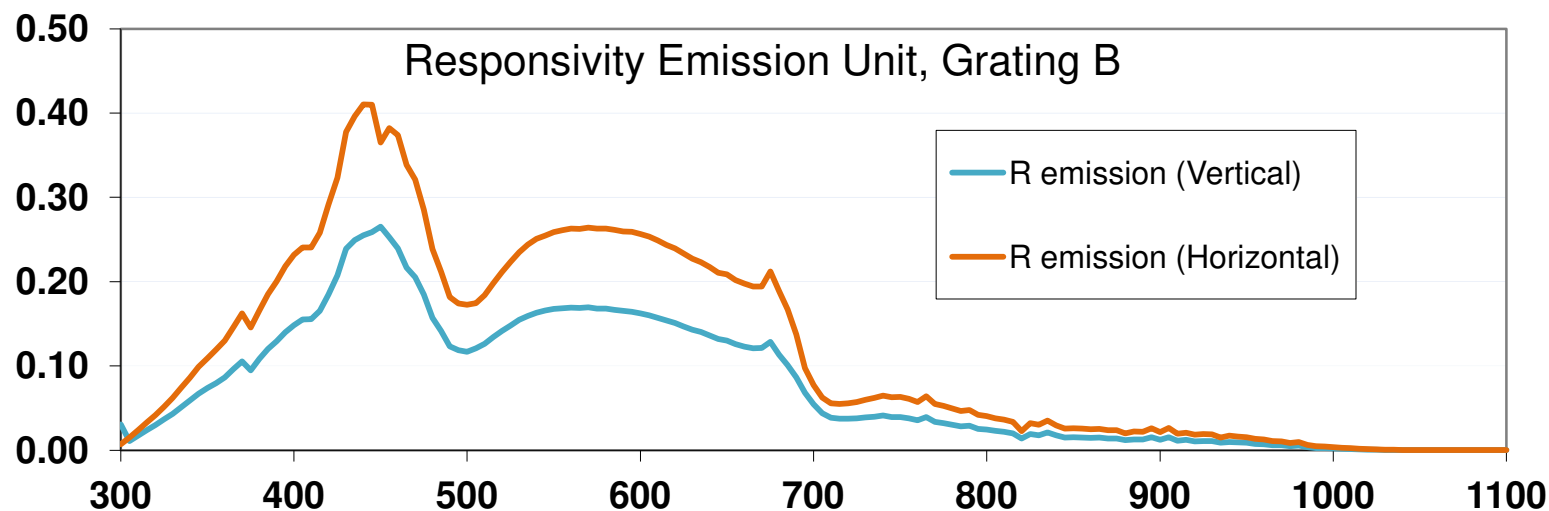
$$R_{sys}(\lambda) = \frac{i_{sw}(\lambda)}{k_2 E_{ref}(\lambda) \beta_{std}(\lambda)}$$



Excitation Unit Spectral
Irradiance, $E_{ref}(\lambda)$



Extension to NIR

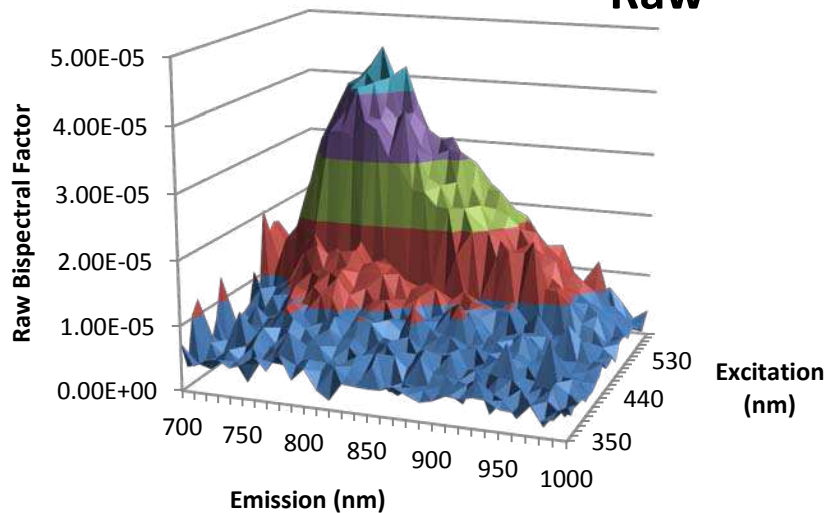




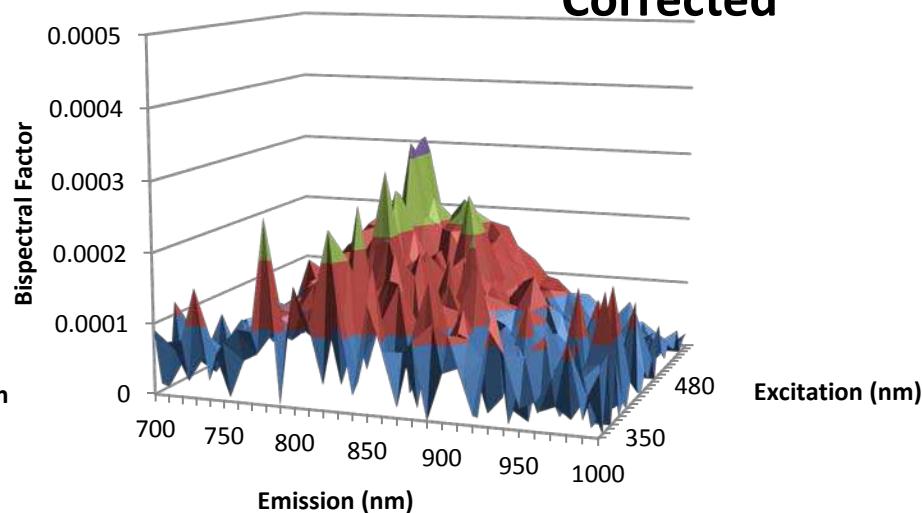
CCS
Orange

Extension to NIR

Raw

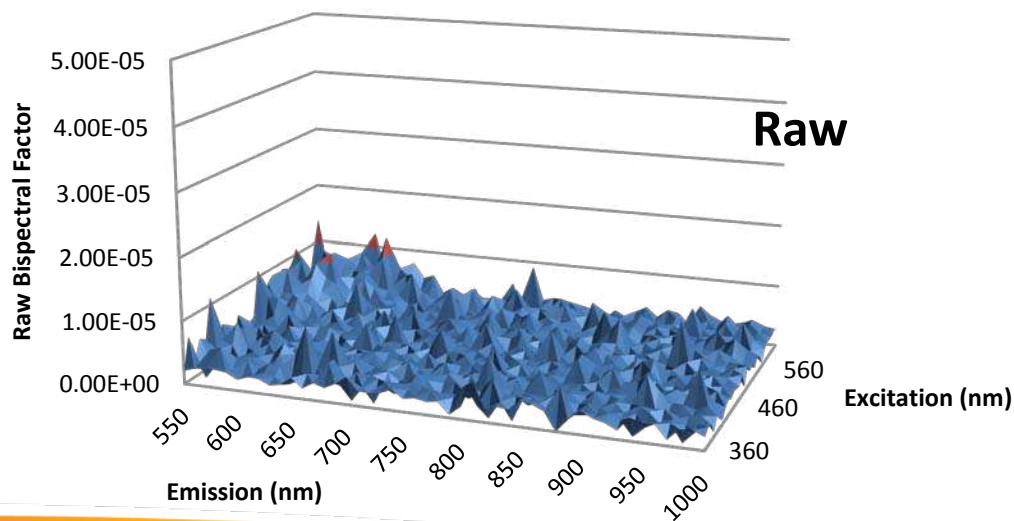


Corrected



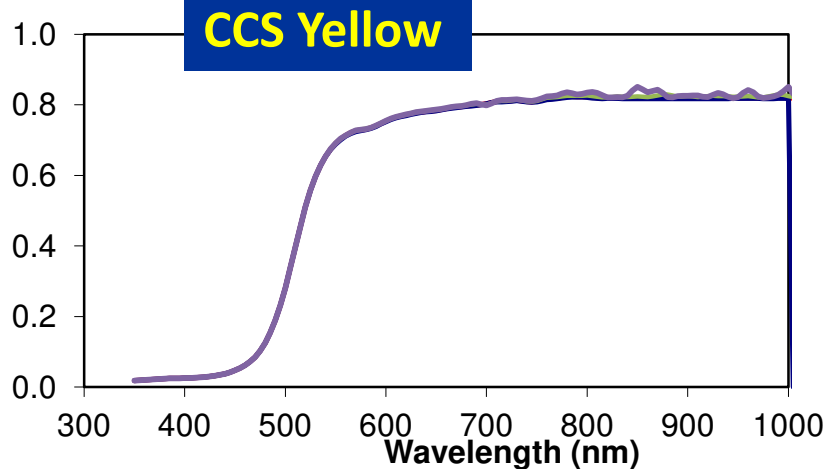
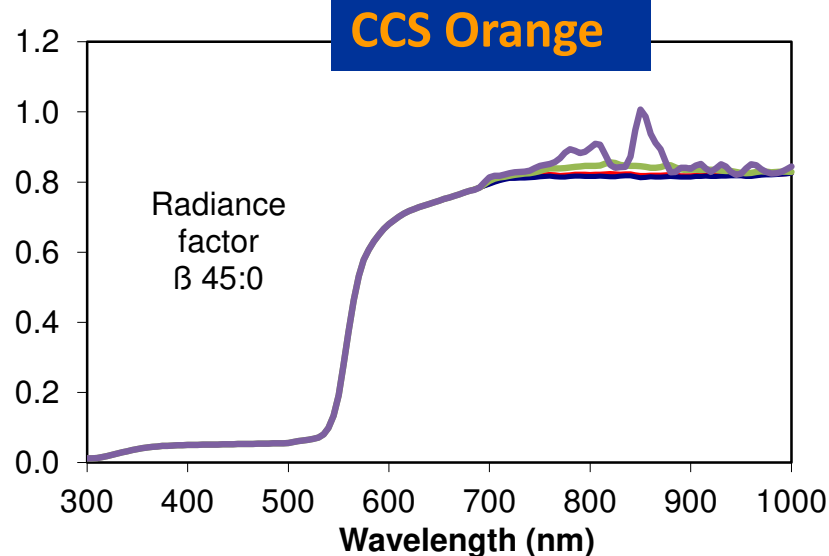
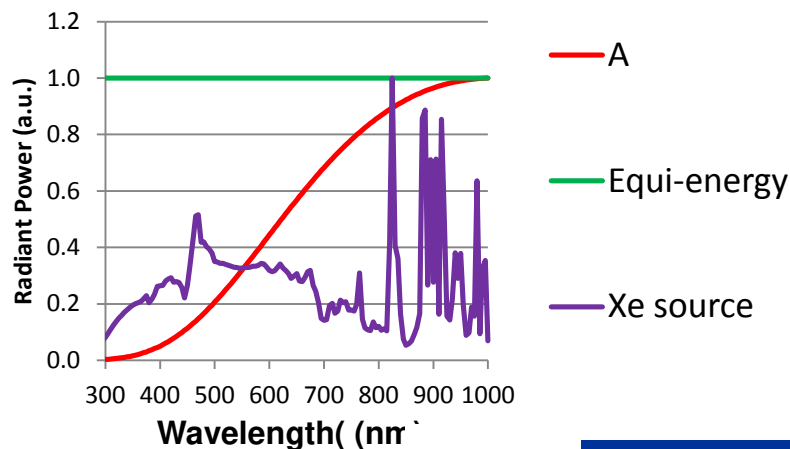
CCS
Yellow

Raw



Impact of NIR Fluorescence

Polychromatic illumination mode



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)

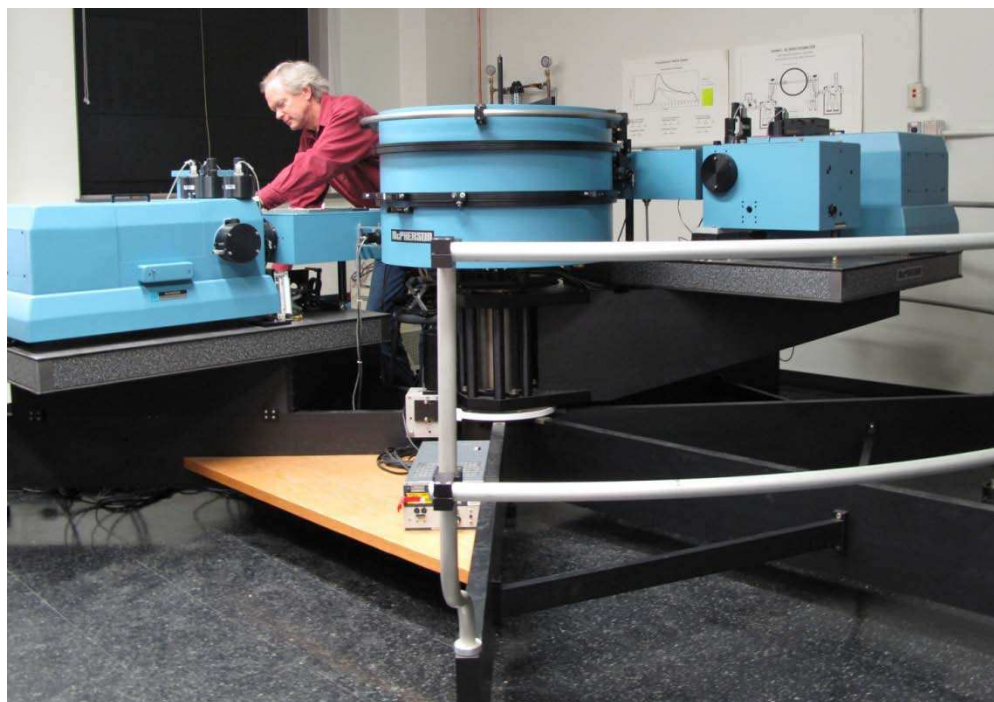
Standardization Procedures

- 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, d:8).

Goniospectrofluorimeter Facility

Gonio – variable angles of incidence and detection

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

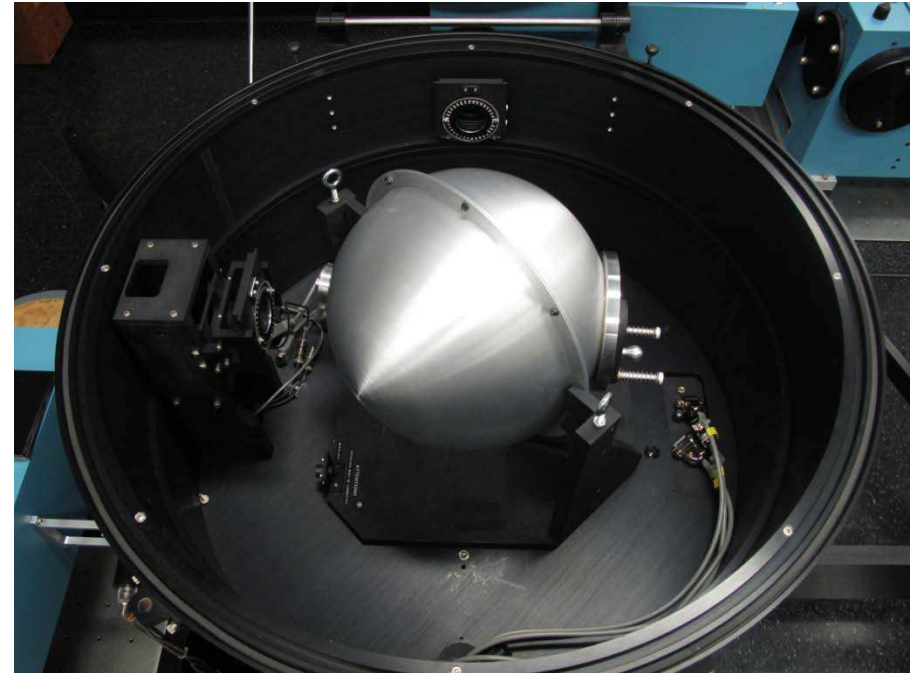
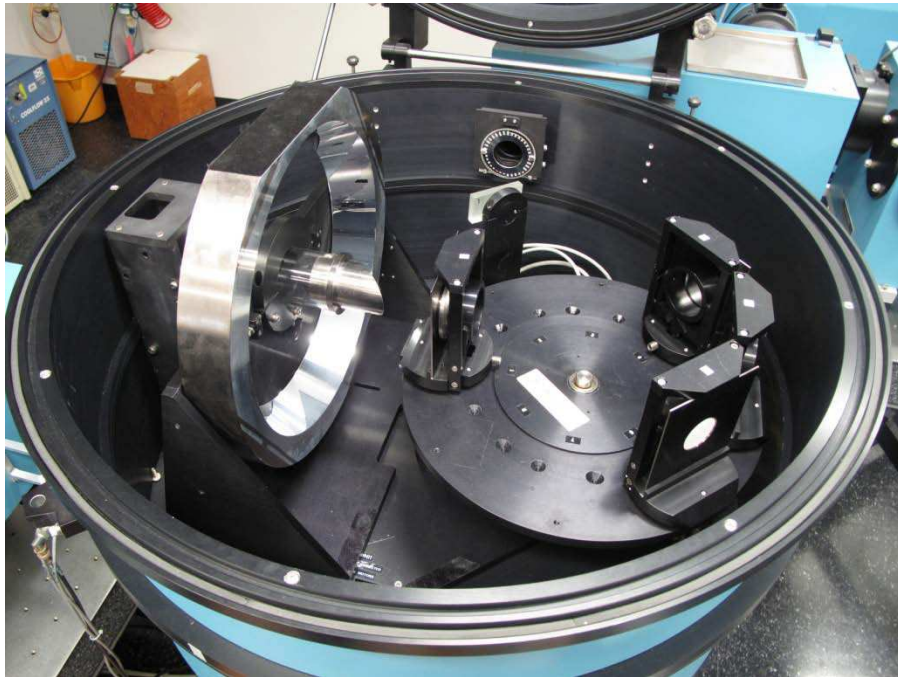


Gonio- spectral fluorescence:

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
(45a:0)

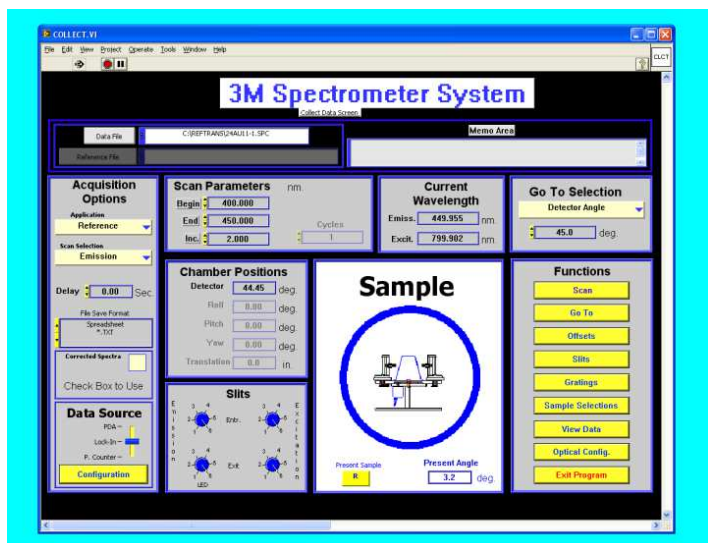


Hemispherical reflectance
(sphere method)

Goniospectrofluorimeter



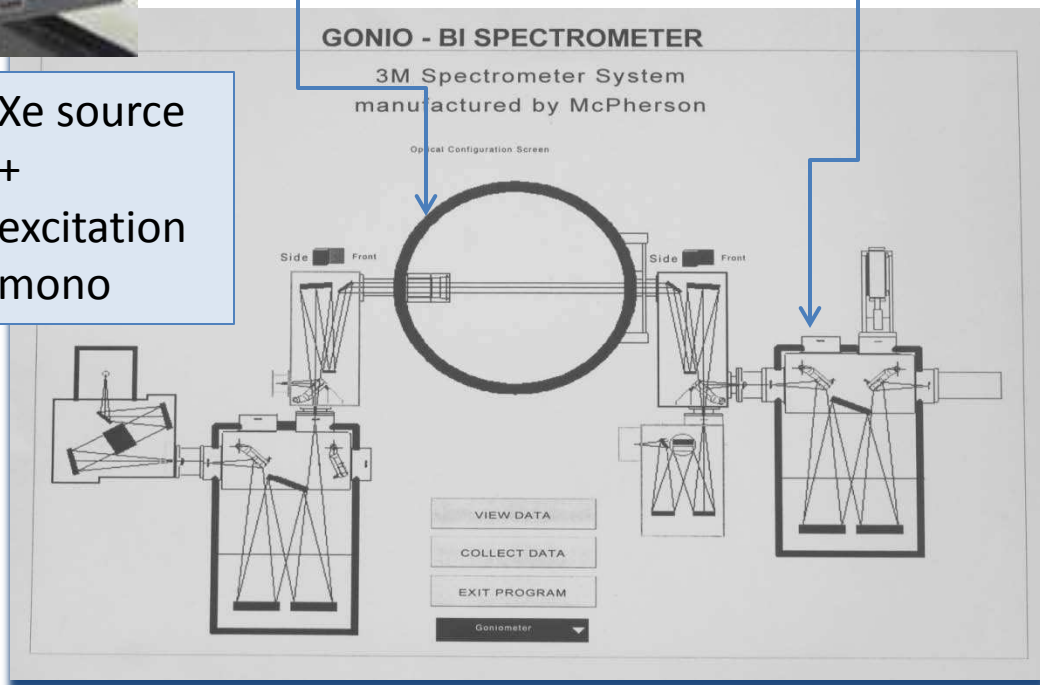
LabView control software



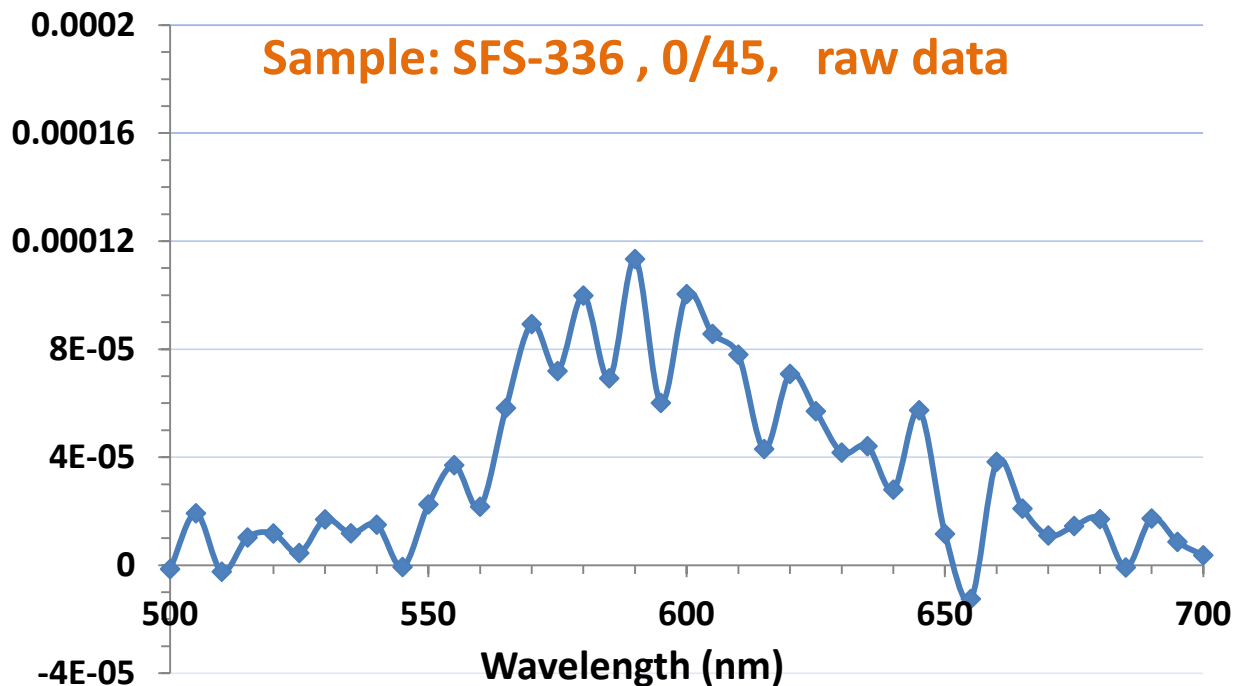
Sample compartment

Emission mono + PMT detector

Xe source + excitation mono



Preliminary NRC Results



$S/N \sim 5:1$

=> Need to
Increase **S**
and
Decrease **N**

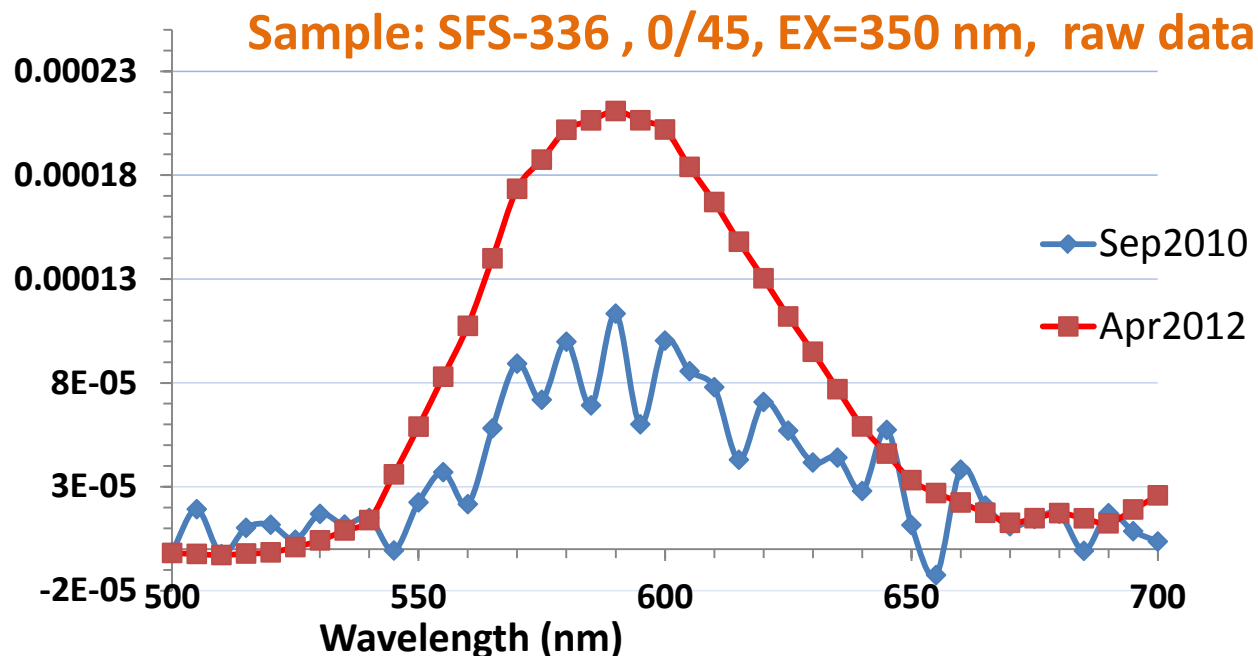
Increase S:

- Re-coat mirrors
- Refurbish predisperser
- Re-optimize optical design
- Improve optical alignment

Decrease N:

- Optimize lock-in operation: phase
- Optimize software :data transfer rate

Current NRC Results



Increase S:

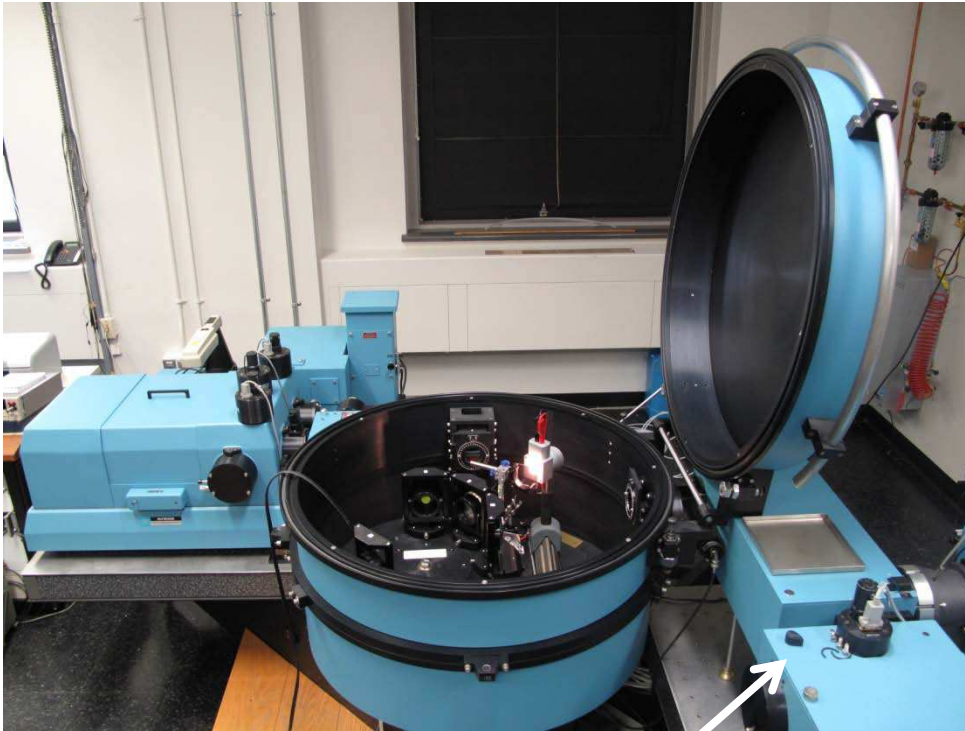
- Change to AR-coated quartz beamsplitter

Decrease N:

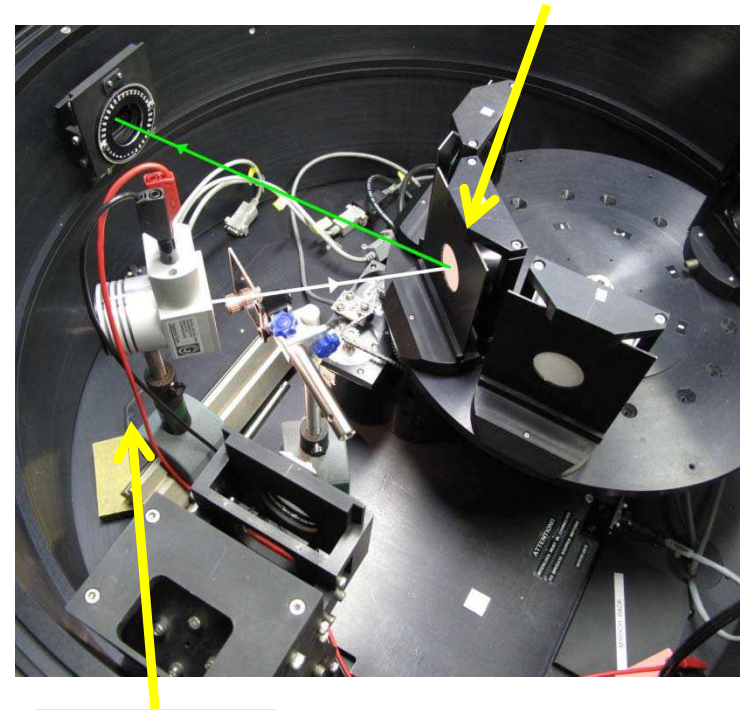
- Add order-sorting filters
- Improve stability of lock-in & chopper method

Calibration of Emission Unit – Calibrated Source Method

Spectral reflectance
standard

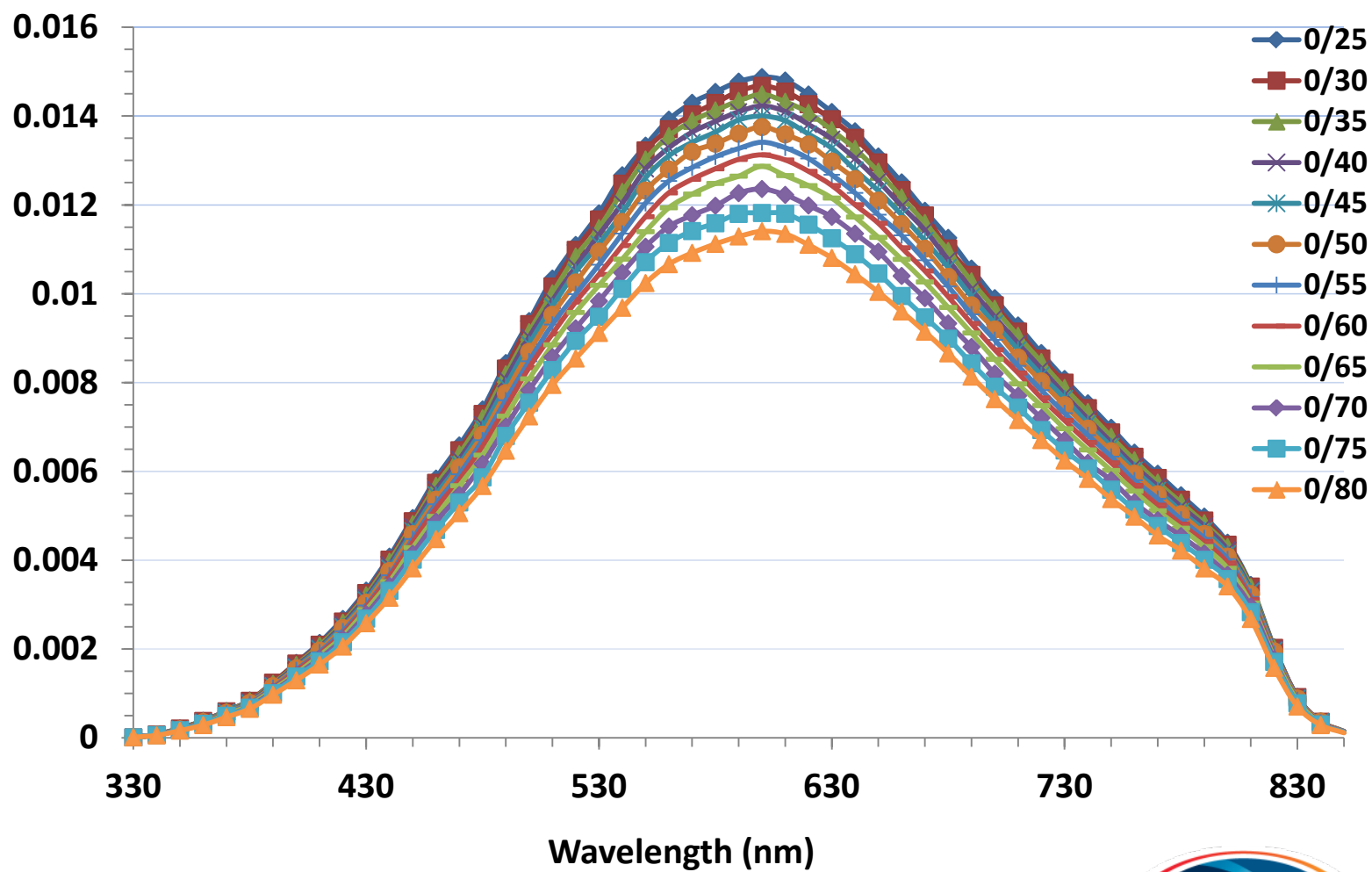


Emission Unit



Spectral
radiance
source

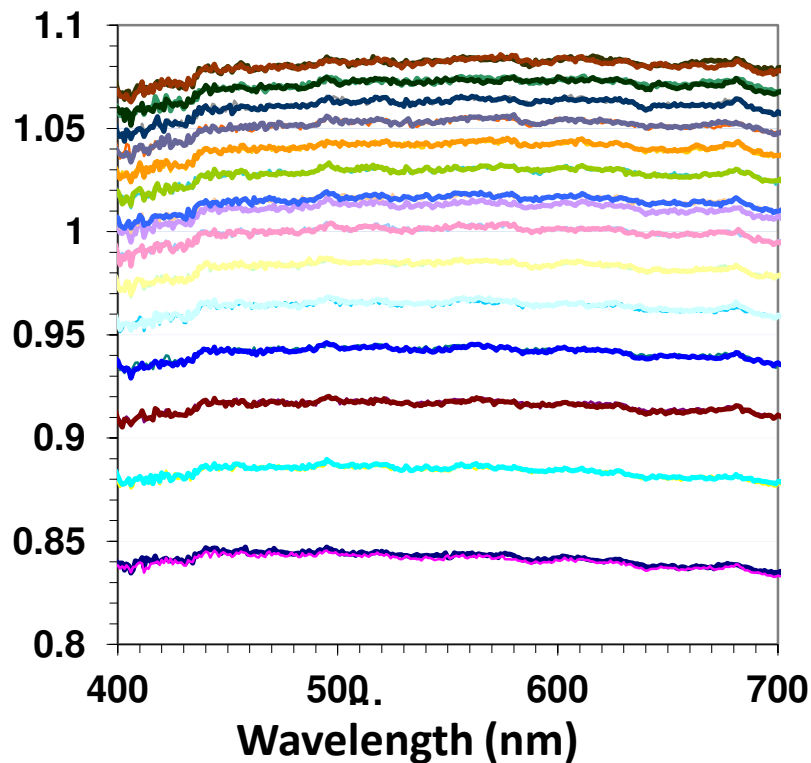
Measured Emission Unit Data (raw)



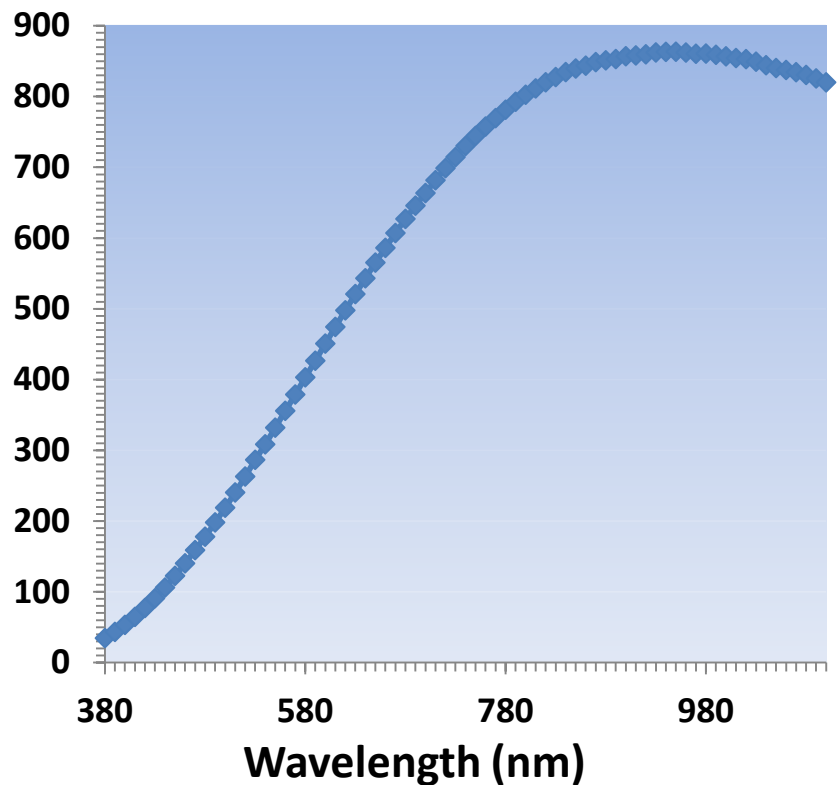
Traceability: Spectral Emission Data

Calibrated spectral reflectance
standard (pressed PTFE)

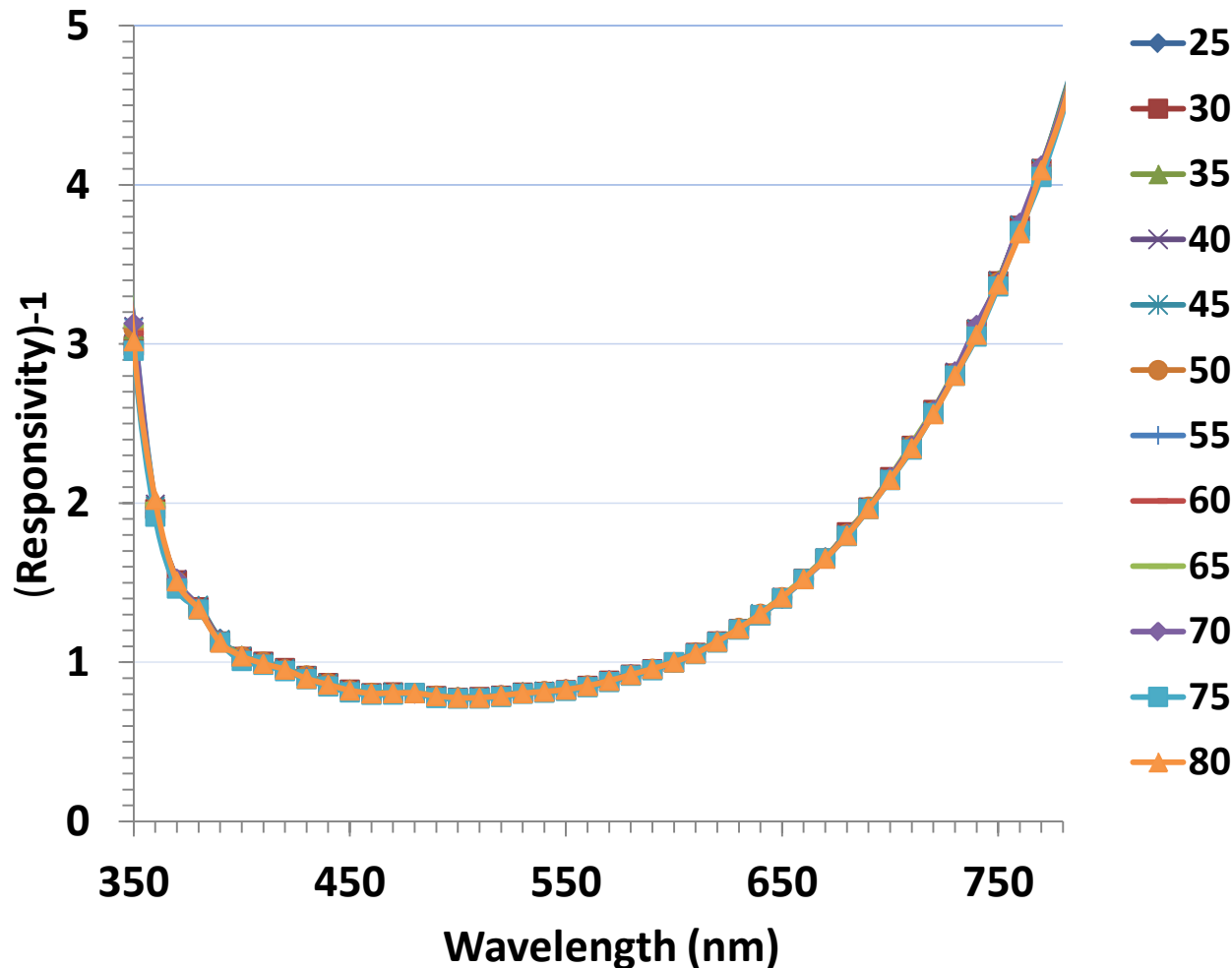
BRDF data: 0/25 to 0/80 degrees



Calibrated spectral radiance
sphere source



Emission Unit Spectral Correction

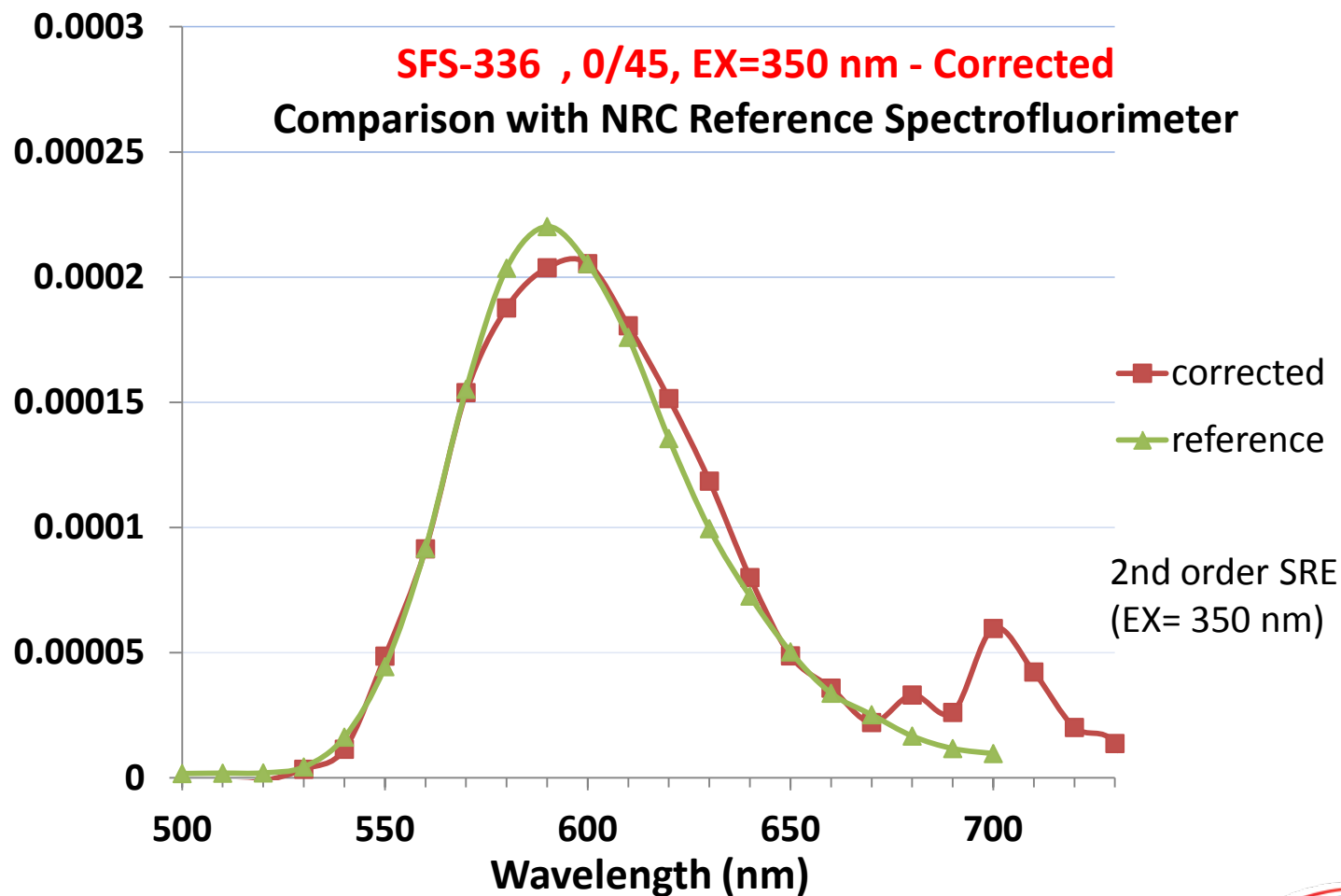


Corrected for:

- Gonio/spectral of PTFE reflectance standard
- Spectral transmittance of ND filter (0.7)
- Standard spectral radiance source

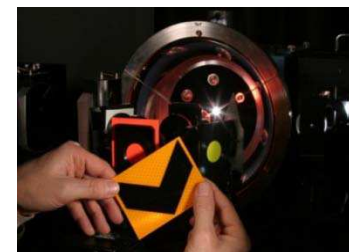
**Spectral Correction –
NOT GEOMETRY-
DEPENDENT**

Current NRC Goniofluorescence Measurement Results



Conclusion

- NRC Fluorescence Project
 - NRC Reference Spectrofluorimeter
 - Routine 45:0 surface fluorescence measurements
- Extension of Capabilities
 - Volume Fluorescence
 - NIR Fluorescence
 - Other Measurement Geometries



Current results are promising



Discussion

Thank-you



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Council Canada

Conseil national
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Canada