Measurement Protocols for Optically Active Pigmented Coatings

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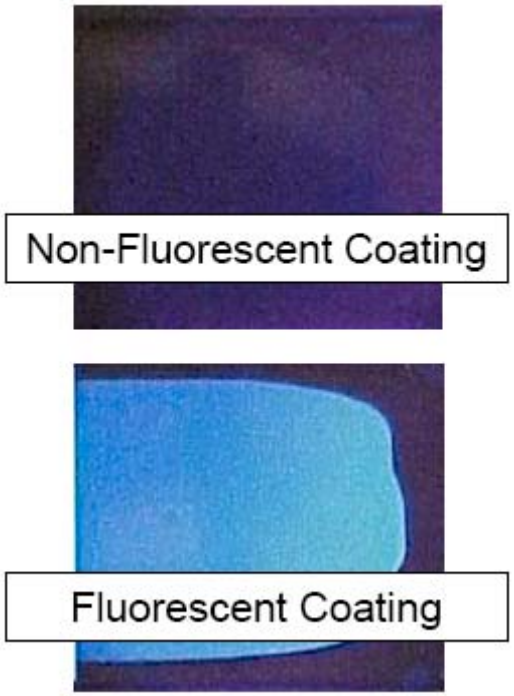
U.S. DOD Corrosion Control

- U.S. Dept. of Defense
  cost of corrosion control $20B/yr
- U.S. Navy corrosion control
  costs $2.4B/yr
- Represervation of tanks
  #1 Fleet maintenance cost

Potential 20 year tank coatings

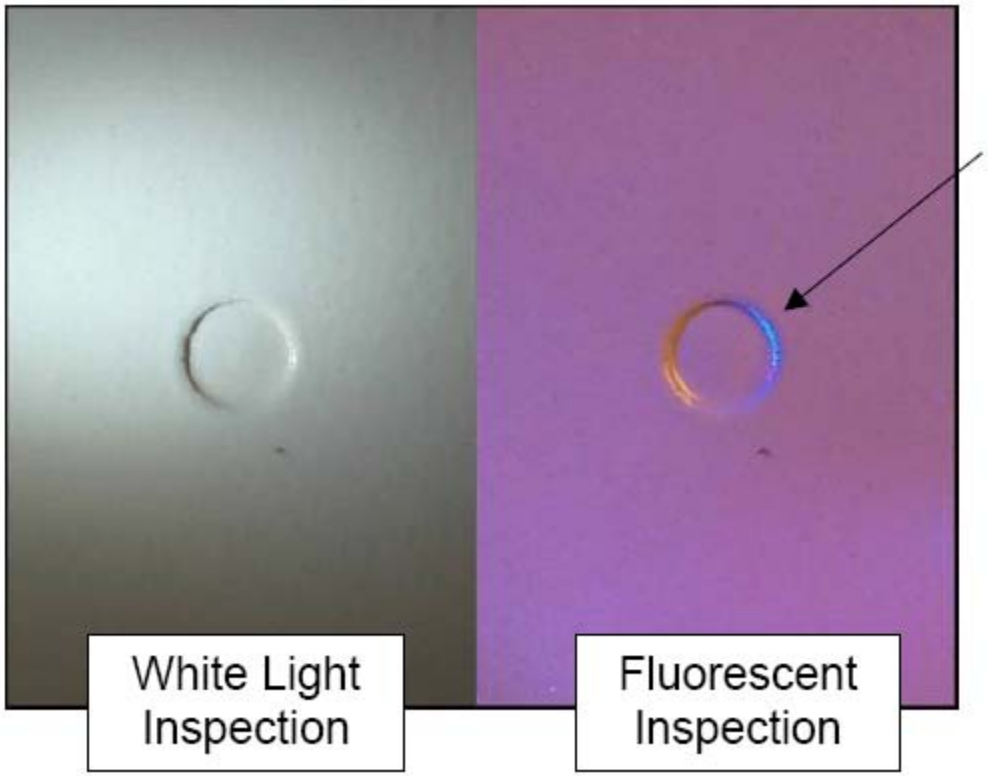
- Holiday free application
- Rigorous QA/QC required

Enhanced Visual Inspection with Fluorescent Coatings



Simple coating change to enhance defect contrast

- Add fluorescent pigment
- Illuminate with Deep Blue light
- Emit intense color



Fluorescent Primer: Specifications

- NAVSEA requires a specification for this fluorescent optical property to use in writing Navy coating contracts
- There is no consistent test method for this fluorescent optical property
- NAVSEA cannot quantify or specify this fluorescent optical property therefore alternate coating suppliers cannot deliver similar coatings

ASTM International

1. Inspection light specification (ASTM E2501-07)
2. Test method for coating luminance contrast (ASTM E12.05 TG7)
3. Coating luminance specification for product qualification (ASTM D01)

Coordination Calibration Group (CCG)**: Project 07-568**

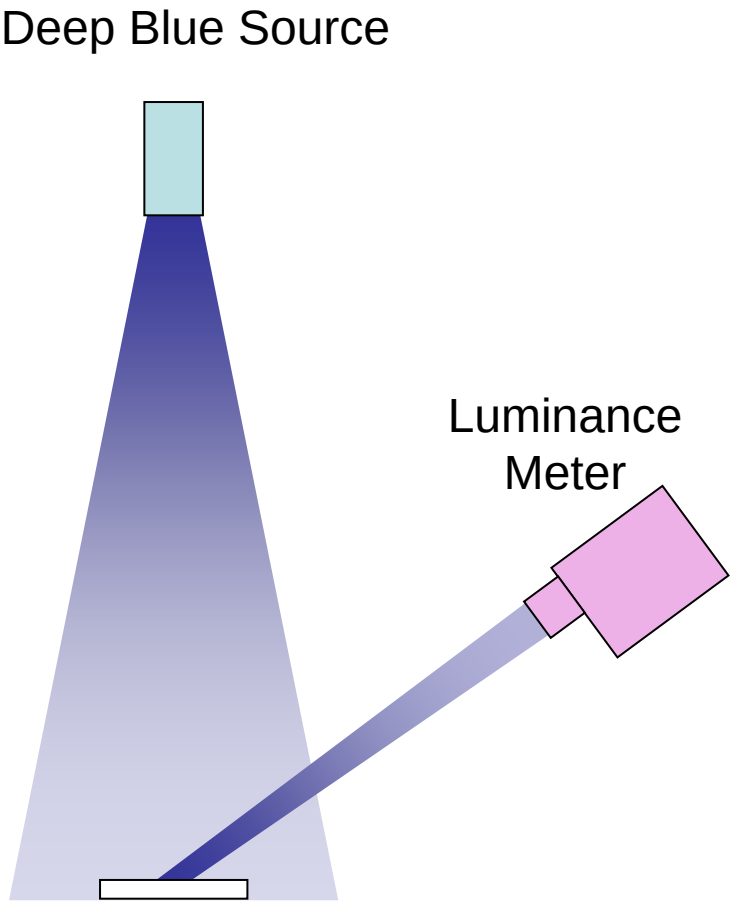
- 35 years the CCG and NIST have provided the military with standards and expertise
- anticipate new technologies and the measurements that they would require
- benefited not only the military services but also American industry

Marie Juliano and Lance Doddridge

Measurement Equation

$$R_L^B = \frac{L^B}{L_P^B}$$

Luminance ratio = luminance of the sample divided by the luminance of a 25 % reflecting Lambertian diffuser under a given deep blue illuminant



Calibrated reference plaque (non-fluorescent) or Test sample (fluorescent)

Measurement Equations

$$L^B = \frac{(s - s_d)}{r \cdot F} \qquad \frac{V}{V/(cd/m^2)} = cd/m^2$$

Sample Luminance = luminance meter signal divided by responsivity of the luminance meter for the spectrum of light emitted from the sample, which is different than the deep blue illuminant

$$L_P^B = \frac{(s_P - s_d)}{r \cdot F_P} \cdot \frac{0.25}{\rho^B} \qquad \frac{V}{V/(cd/m^2)} = cd/m^2$$

Reference Luminance = luminance meter signal divided by responsivity of the luminance meter for the deep blue illuminant multiplied by the 25 % reflecting Lambertian diffuser divided by the calibrated reflectance of the standard under the deep blue illuminant

Uncertainty Components

$$R_L^B = \frac{\frac{(s - s_d)}{r \cdot F}}{\frac{(s_P - s_{P,d})}{r \cdot F_P} \cdot \frac{0.25}{\rho^B}} \rightarrow \frac{(s - s_d)}{(s_P - s_{P,d})} \cdot \frac{F_P}{F} \cdot \frac{\rho^B}{0.25} \cdot C_f$$

s_P	– reference signal
$s_{P,d}$	– reference dark signal
s	– sample signal
s_d	– sample dark signal
F_P	– spectral mismatch correction of responsivity reference signal
F	– spectral mismatch correction of responsivity sample signal
ρ^B	– luminance reflectance of calibrated reference standard

Uncertainty Components

$$R_L^B = \frac{(s - s_d)}{(s_P - s_{P,d})} \cdot \frac{F_P}{F} \cdot \frac{\rho^B}{0.25} \cdot C_f$$

λ_B	– wavelength dependence
$\Delta\lambda_B$	– illumination bandwidth dependence
λ_S	– spectral out-of-band light (fluorescence from source)
S	– out-of-band stray light (inside detector)
L	– linearity of the detector
O	– Out-of-field sensitivity of the luminance meter
c_s	– voltmeter calibration
ϕ_P	– incident angle of light on reference
ϕ	– incident angle of light on sample
θ_P	– viewing angle of light from reference
θ	– viewing angle of light from sample

Uncertainty Components

$$R_L^B = \frac{(s - s_d)}{(s_P - s_{P,d})} \cdot \frac{F_P}{F} \cdot \frac{\rho^B}{0.25} \cdot C_f$$

U_L – uniformity of the light source

U_P – uniformity of the reference material

U – uniformity of the sample material

U_r – uniformity of the detector responsivity

T_P – temperature dependence of the reference material

T – temperature dependence of the sample material

T_r – temperature dependence of the luminance meter responsivity

P_P – polarization dependencies of the reference material

P – polarization dependencies of the sample material

P_r – polarization dependencies of the luminance meter

I – deviation from the inverse square law

Tolerance Propagation Equation

(from ASTM D4356)

$$\frac{\Delta R^2}{2} = \sum_{i=1}^{q} \left(\frac{\partial R}{\partial X_i} \right)^2 \Delta X_i^2$$

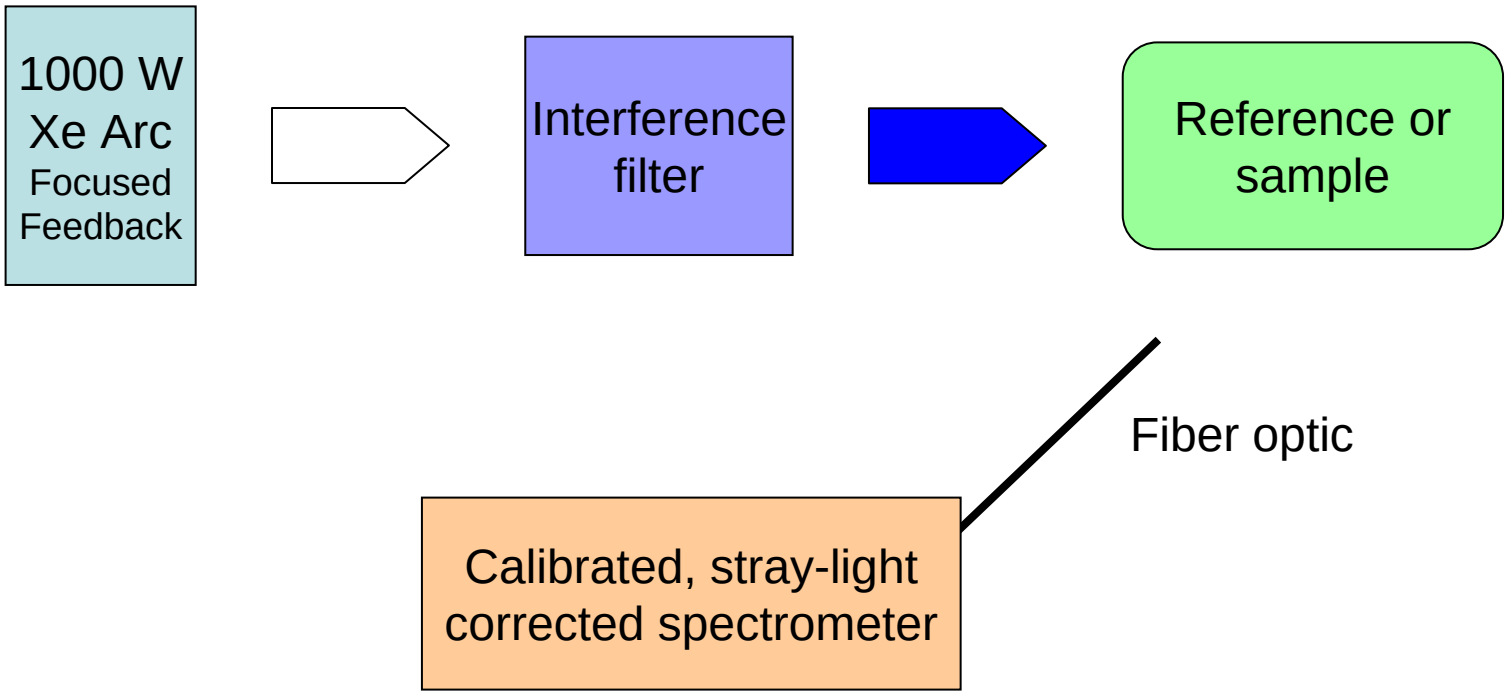
X_i	= the measurement value
ΔX_i	= the specified measurement tolerance
R	= the determination value
ΔR	= the determination tolerance
$\frac{\partial R}{\partial X_i}$	= the sensitivity coefficient

X_i is the mean of a rectangular distribution and ΔX_i is the range of the distribution

98.6 % probability level the determination value, R, is within the range ΔR

Wavelength Dependence

Goal: Determine sensitivity coefficient between excitation wavelength and R_L^B



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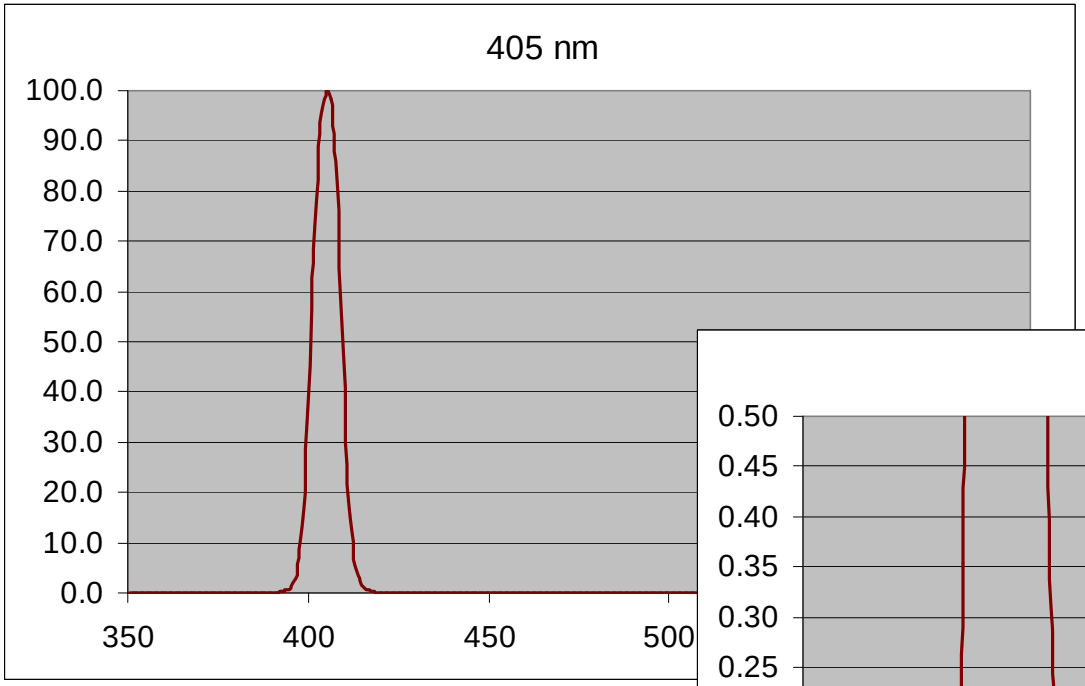

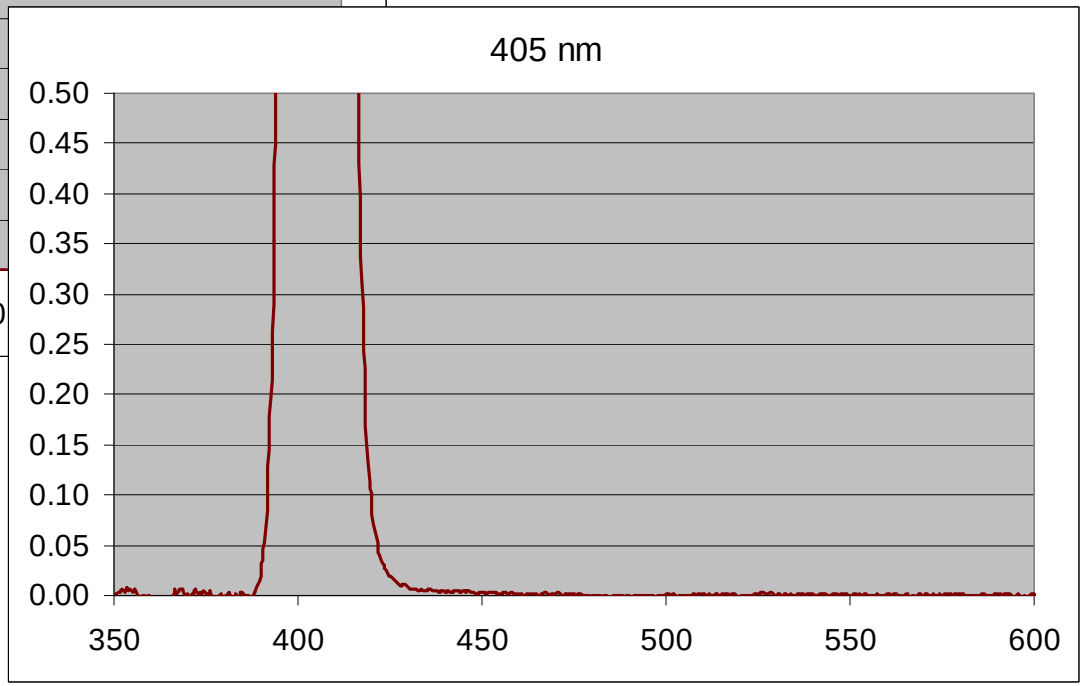

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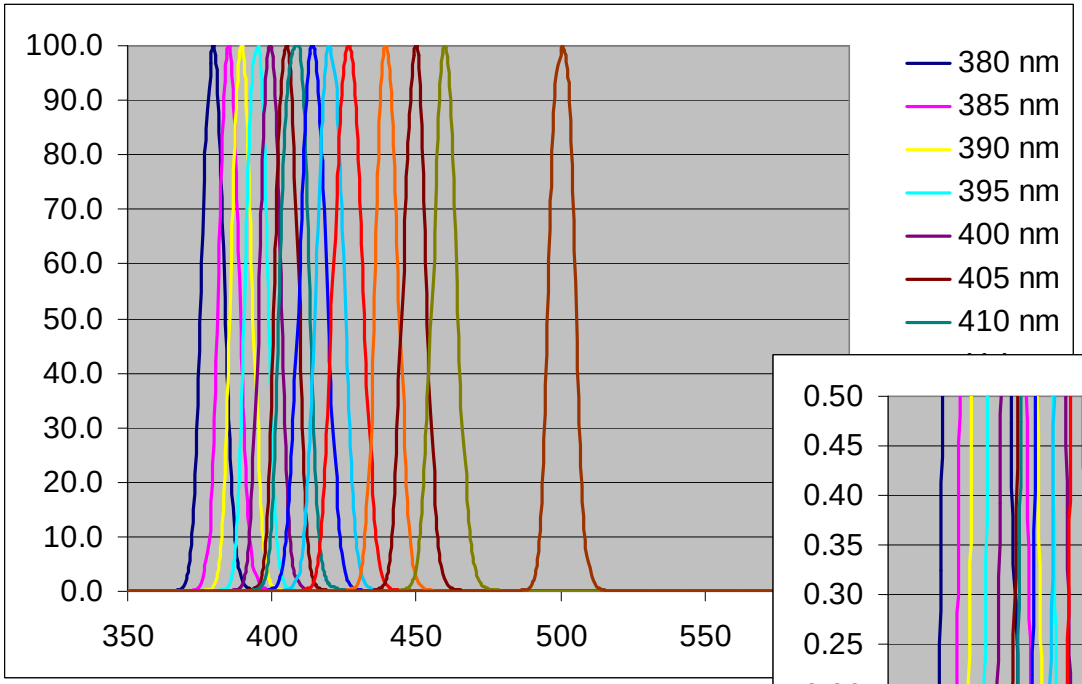
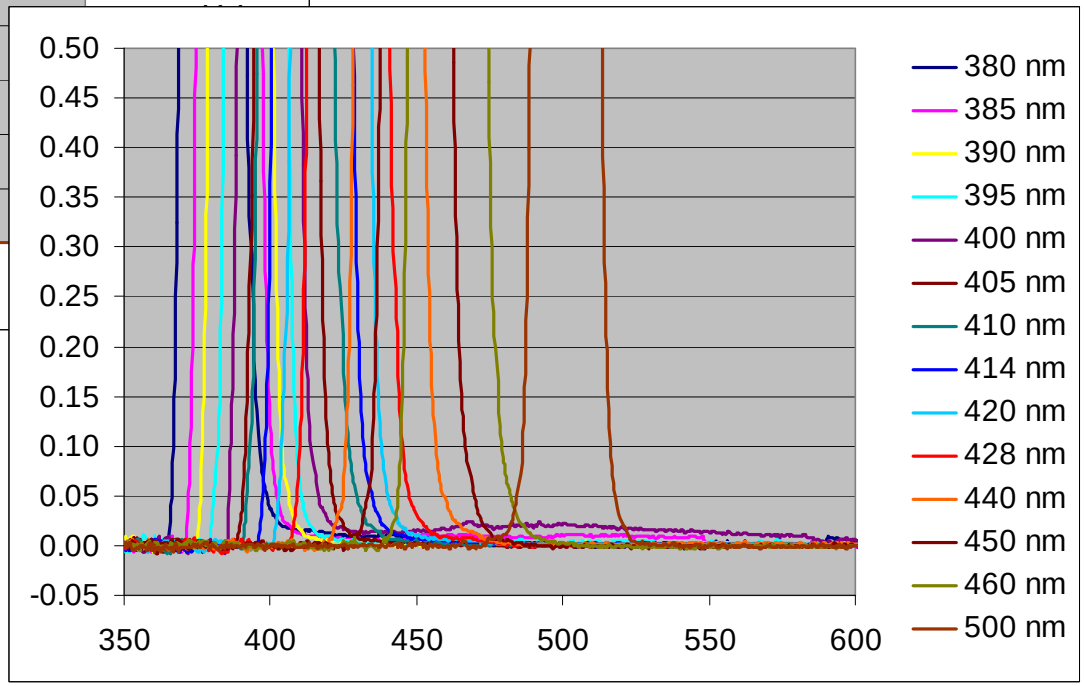


E2501-07	% < 450 nm
390 nm – 100 %	410 nm – 100 %
395 nm – 100 %	414 nm – 100 %
400 nm – 100 %	420 nm – 100 %
405 nm – 100 %	



% Visible	
390 nm – 0.04 %	405 nm – 0.02 %
395 nm – 0.06 %	410 nm – 0.02 %
400 nm – 0.28 %	414 nm – 0.05 %
	420 nm – 0.10 %

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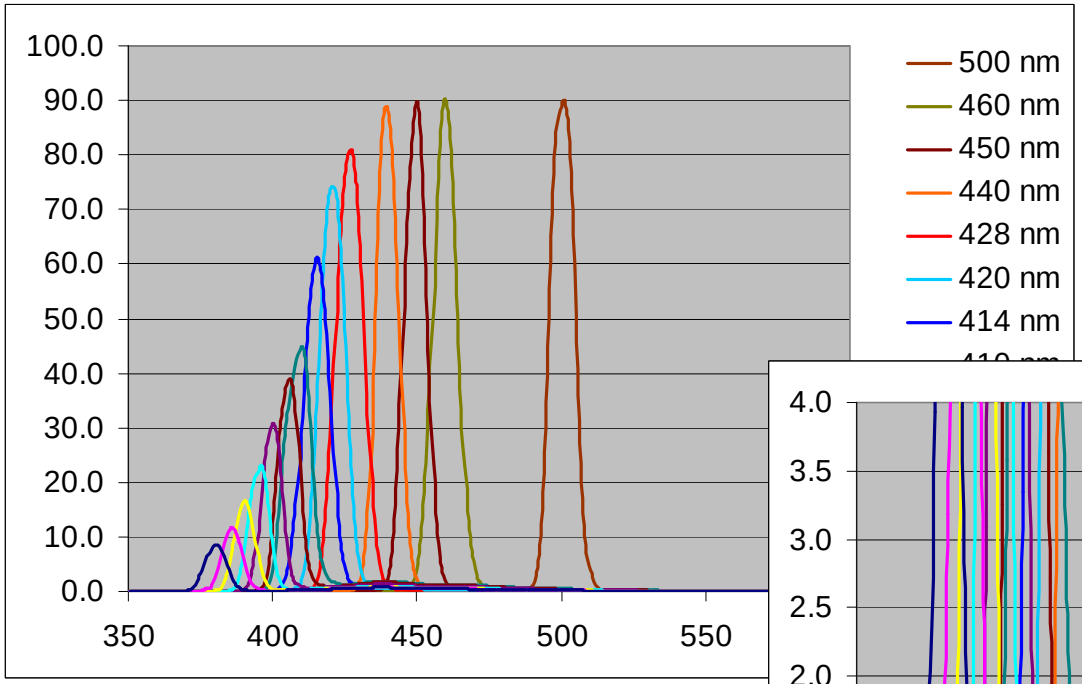
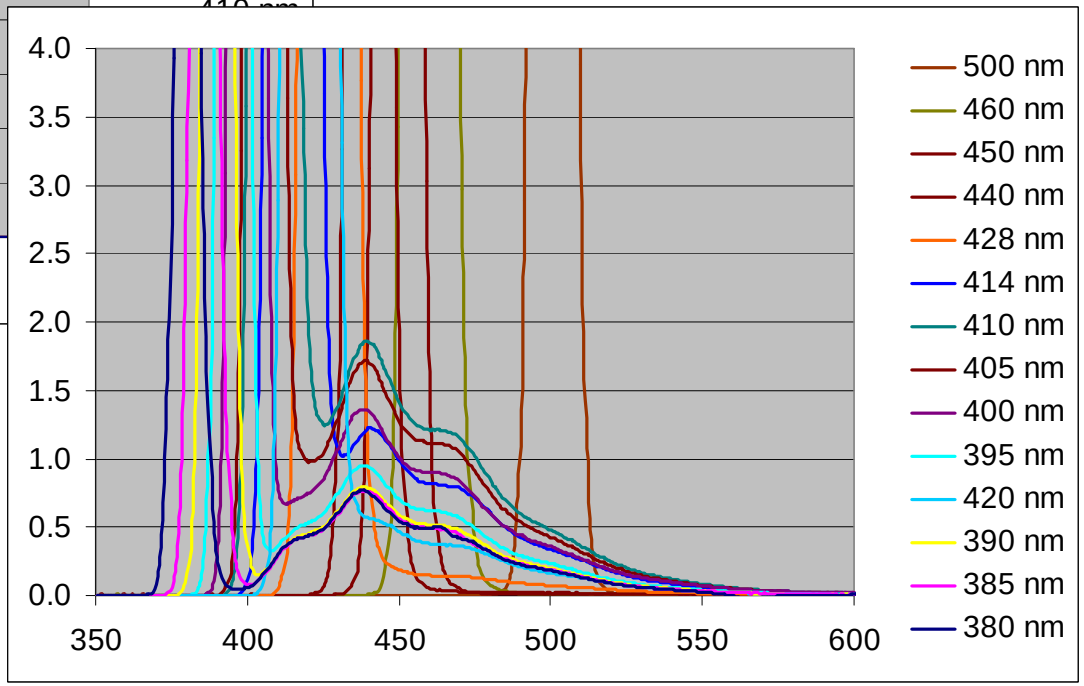


Sample 210



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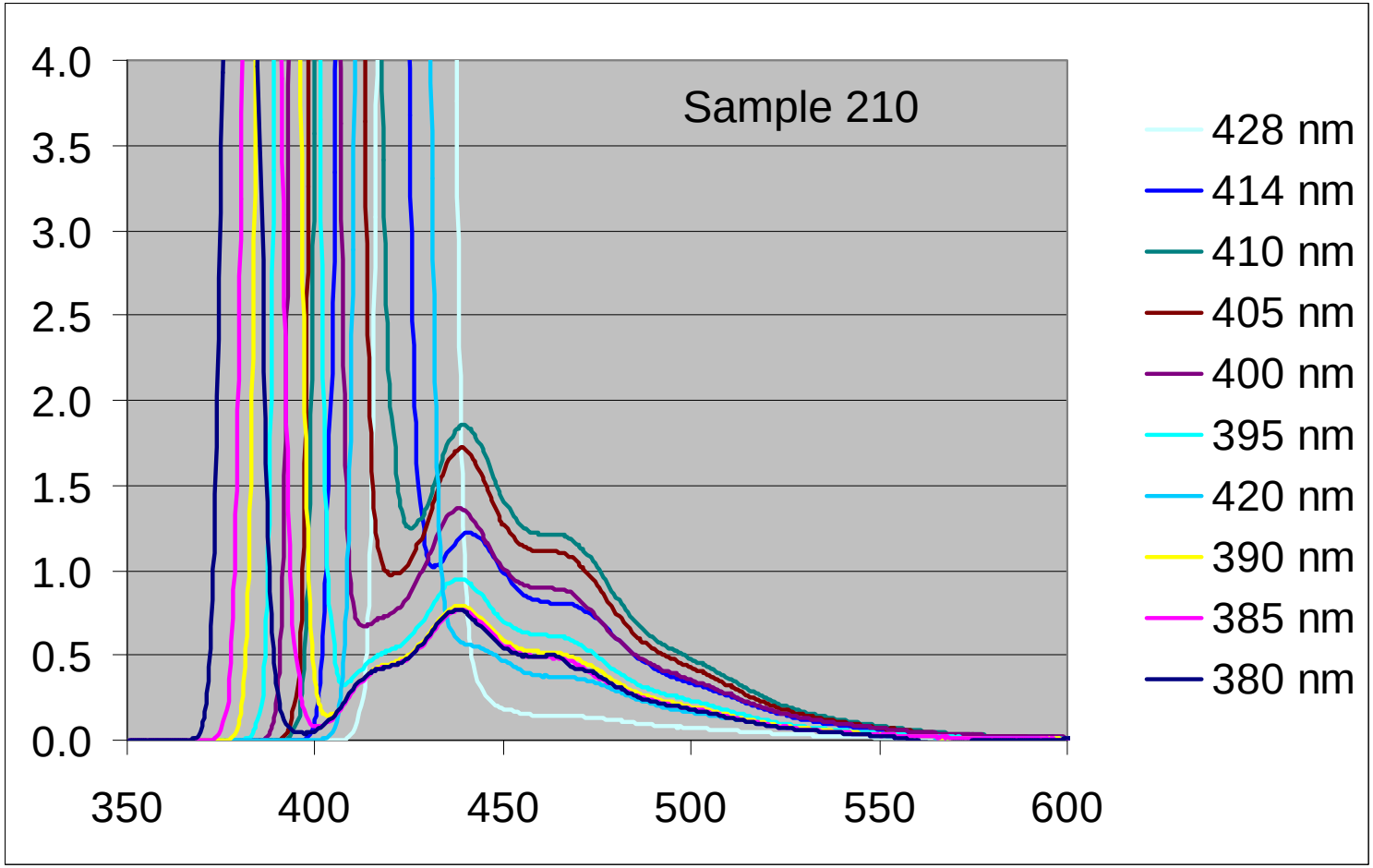

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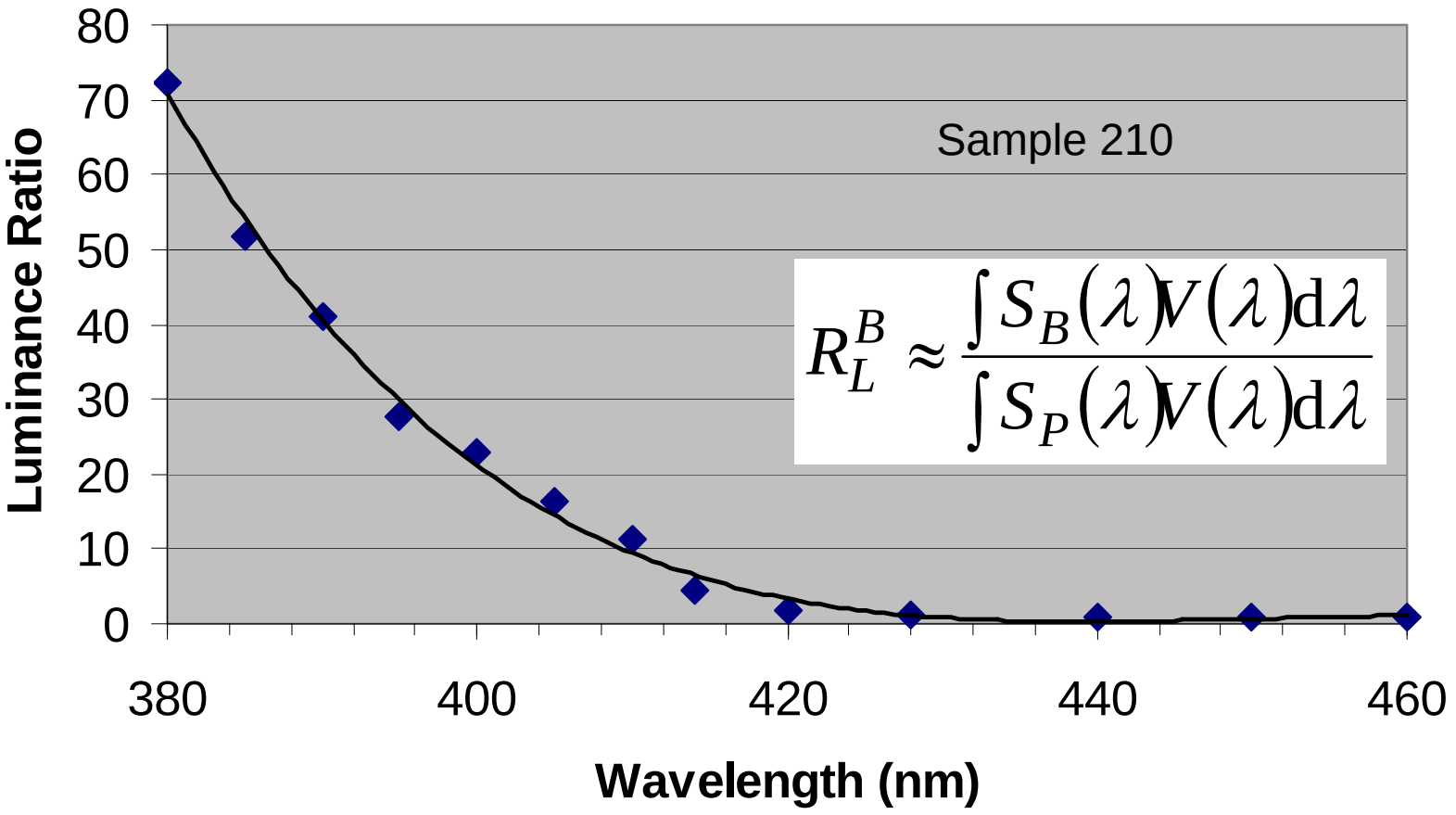

Sensitivity coefficient → -7 % per nanometer

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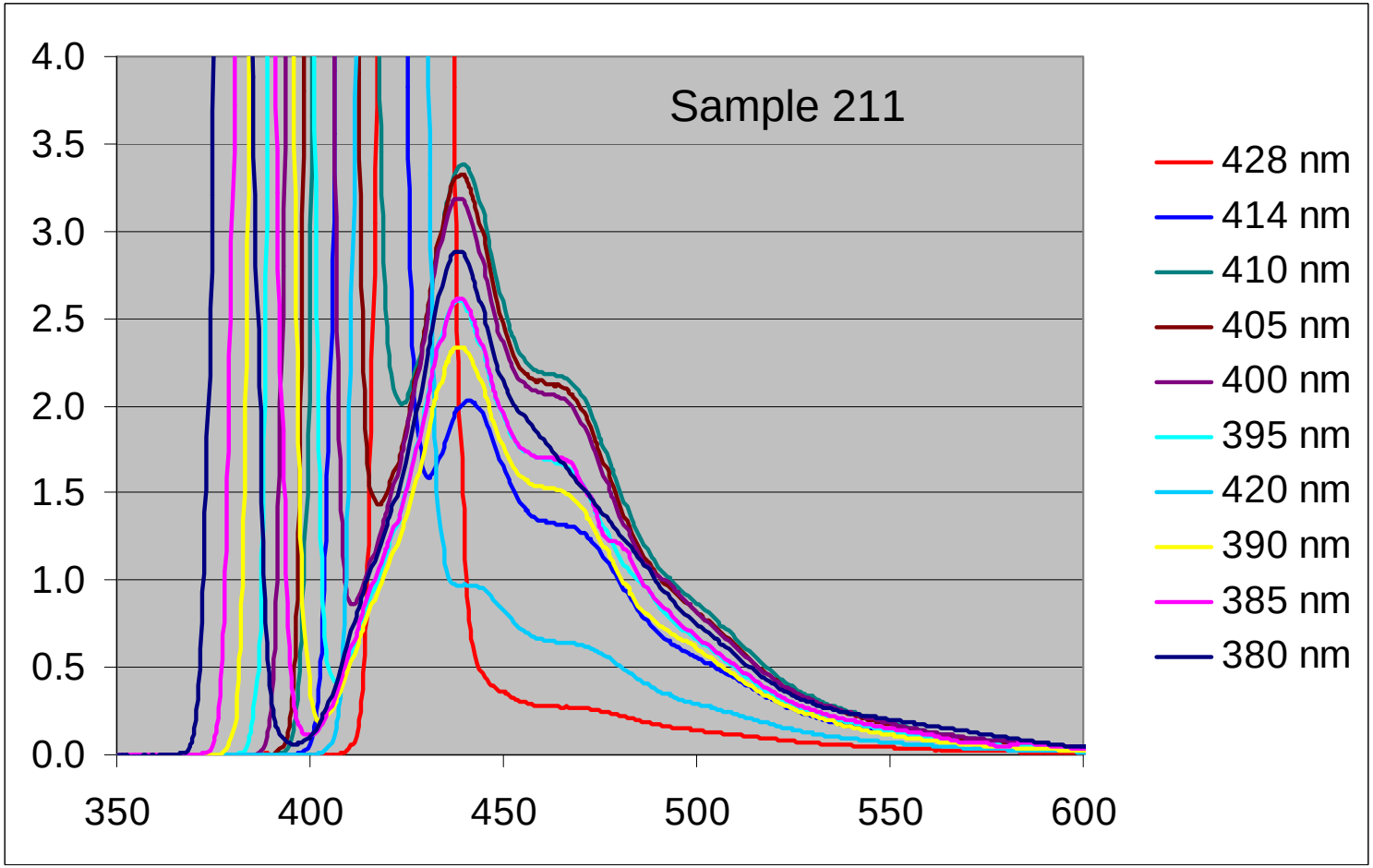

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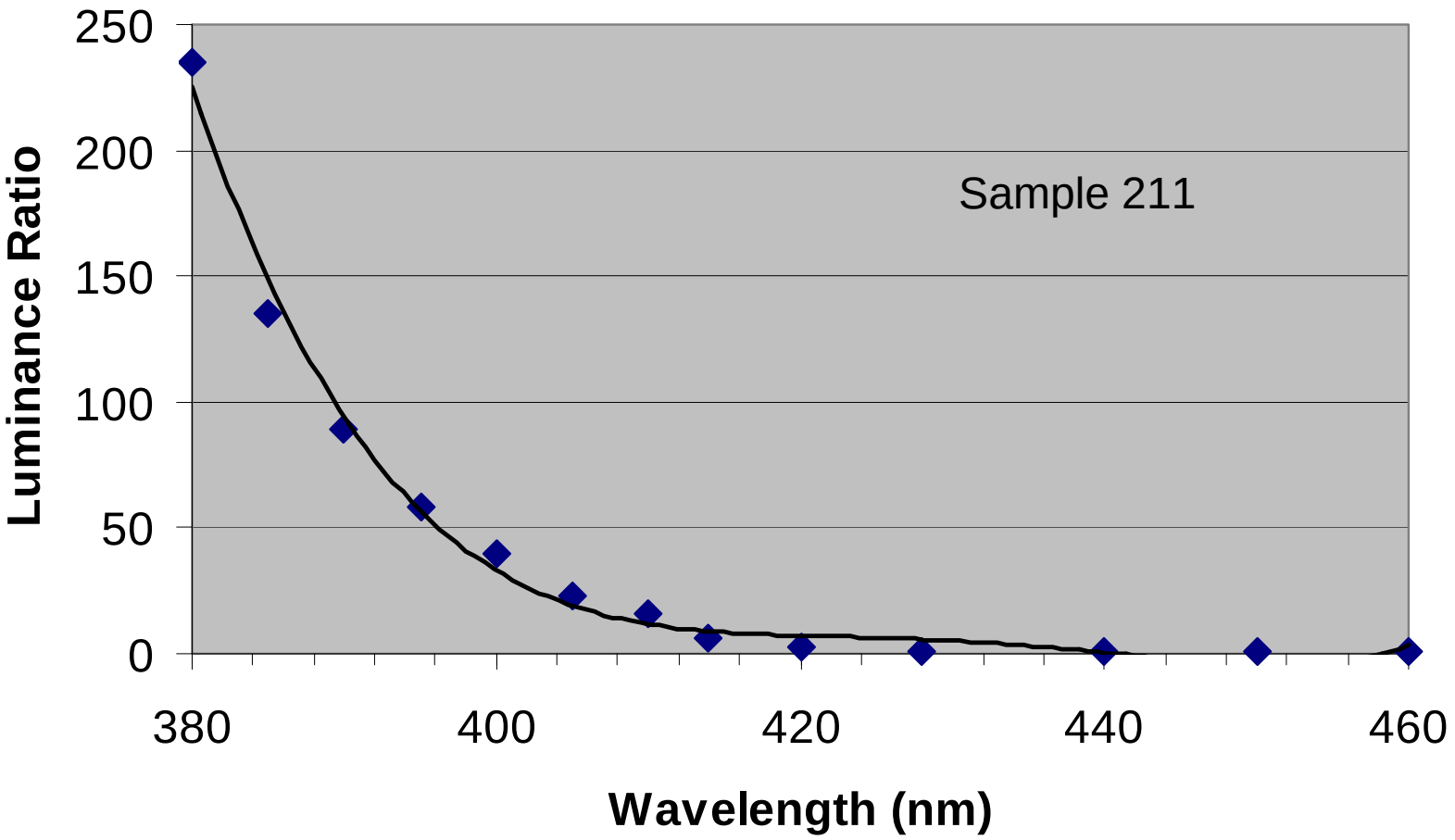


Sensitivity coefficient → -10.0 % per nanometer

Wavelength Dependence

Goal: Determine sensitivity coefficient between excitation wavelength and R_L^B

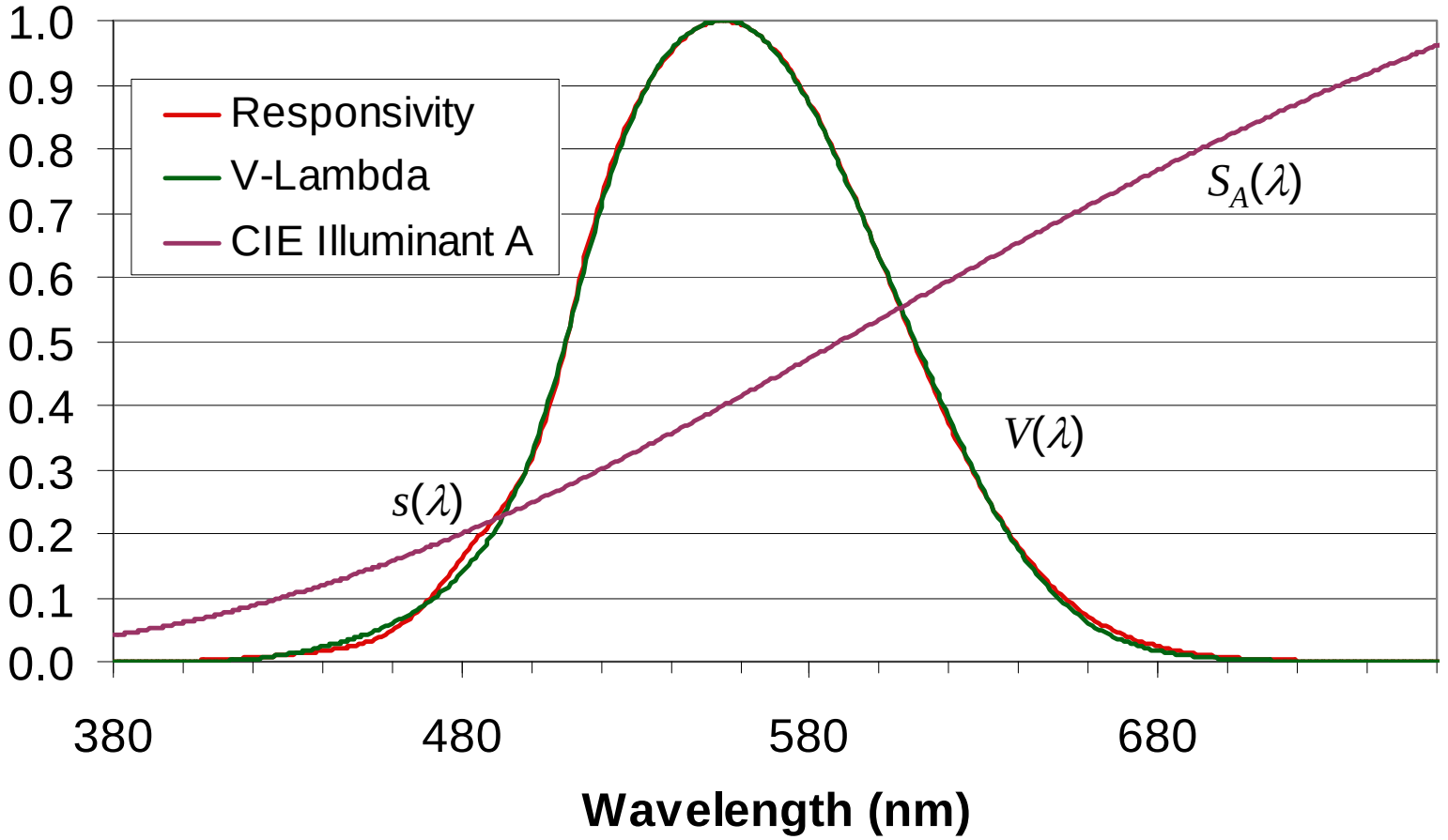
$$\frac{\Delta R^2}{2} = \sum_{i=1}^{q} \left(\frac{\partial R}{\partial X_i} \right)^2 \Delta X_i^2$$

$$\frac{\partial R_L^B}{\partial \lambda} = \frac{-10\%}{nm} \quad \text{and} \quad \Delta\lambda = 2\,nm$$

404 nm – 406 nm

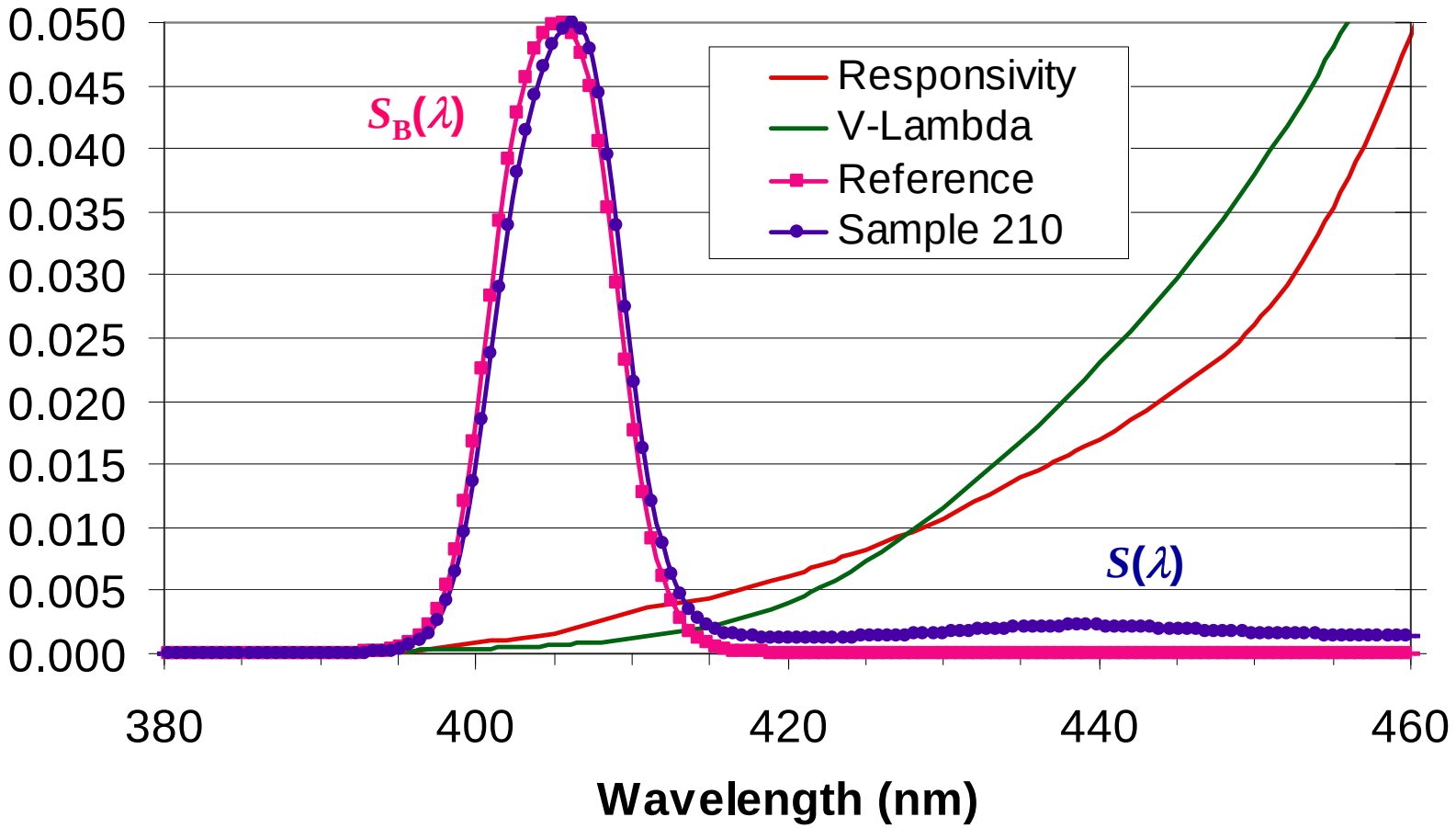
$$\frac{\Delta R_L^B}{R_L^B} = 28\,\%$$

Spectral Mismatch Correction, F



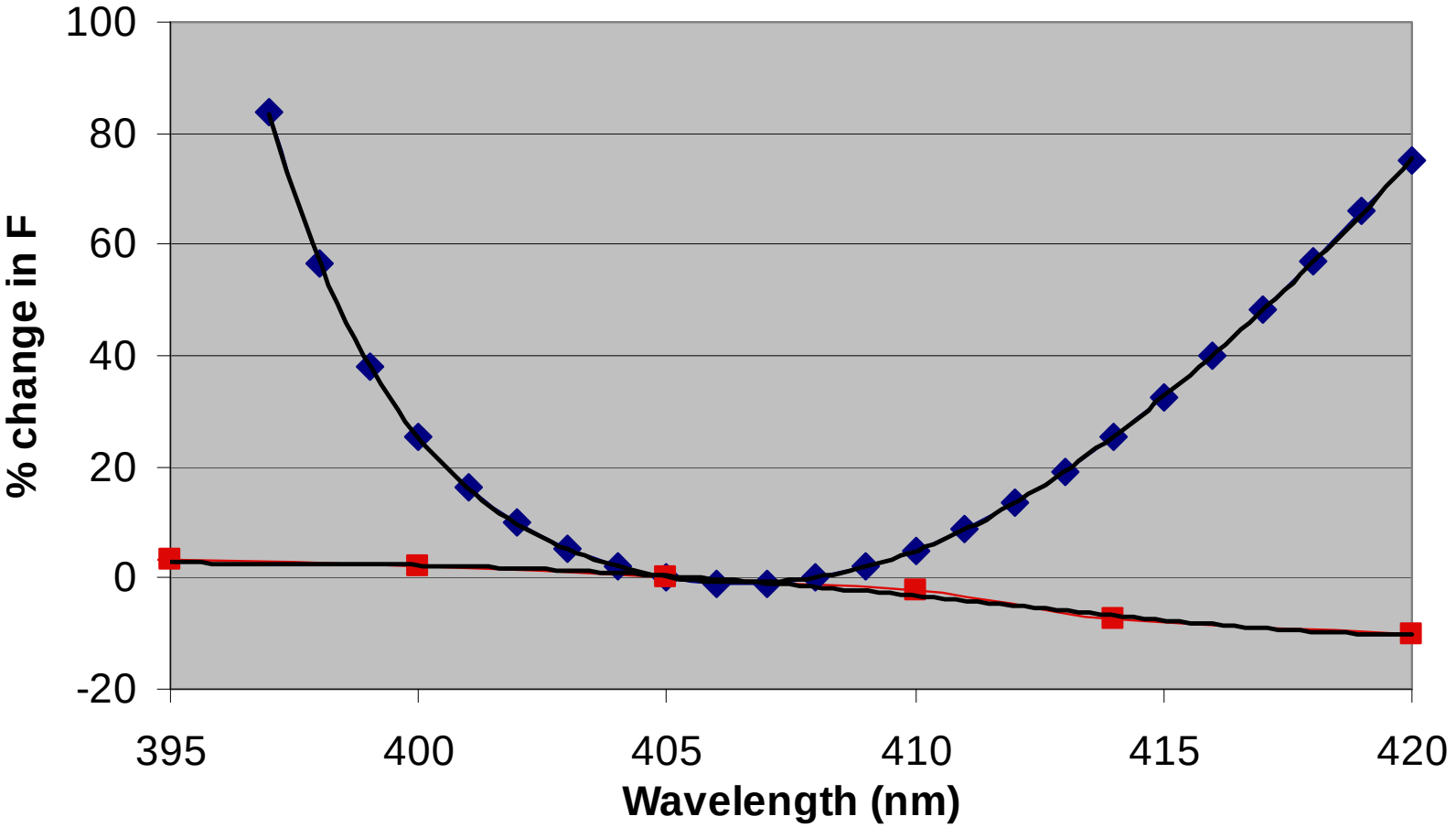
$$F_P = \frac{\int_\lambda S_A(\lambda)s(\lambda)\mathrm{d}\lambda}{\int_\lambda S_A(\lambda)V(\lambda)\mathrm{d}\lambda} \cdot \frac{\int_\lambda S_B(\lambda)V(\lambda)\mathrm{d}\lambda}{\int_\lambda S_B(\lambda)s(\lambda)\mathrm{d}\lambda}$$

Spectral Mismatch Correction, F



$$F_P = 0.321 \quad F = 0.984$$

Spectral Mismatch Correction



$$\frac{\partial F_P}{\partial \lambda} = \frac{-2.4\%}{nm} \quad \text{and} \quad \frac{\partial F}{\partial \lambda} = \frac{-0.6\%}{nm}$$

Spectral Mismatch Correction

$$\frac{\partial F_P}{\partial \lambda} = \frac{-2.4\%}{nm} \quad \text{and} \quad \frac{\partial F}{\partial \lambda} = \frac{-0.6\%}{nm} \qquad \Delta\lambda = 2\,nm$$

$$\frac{\Delta F_P}{F_P} = 6.8\,\% \quad \text{and} \quad \frac{\Delta F}{F} = 1.7\%$$

$F_P = 0.321$

$\Delta F_P = 0.022$

$R_L^B = 15.23$

$\frac{\partial R_L^B}{\partial F_P} = 47.45$

$\frac{\Delta R_L^B}{R_L^B} = 9.6\,\%$

$F = 0.984$

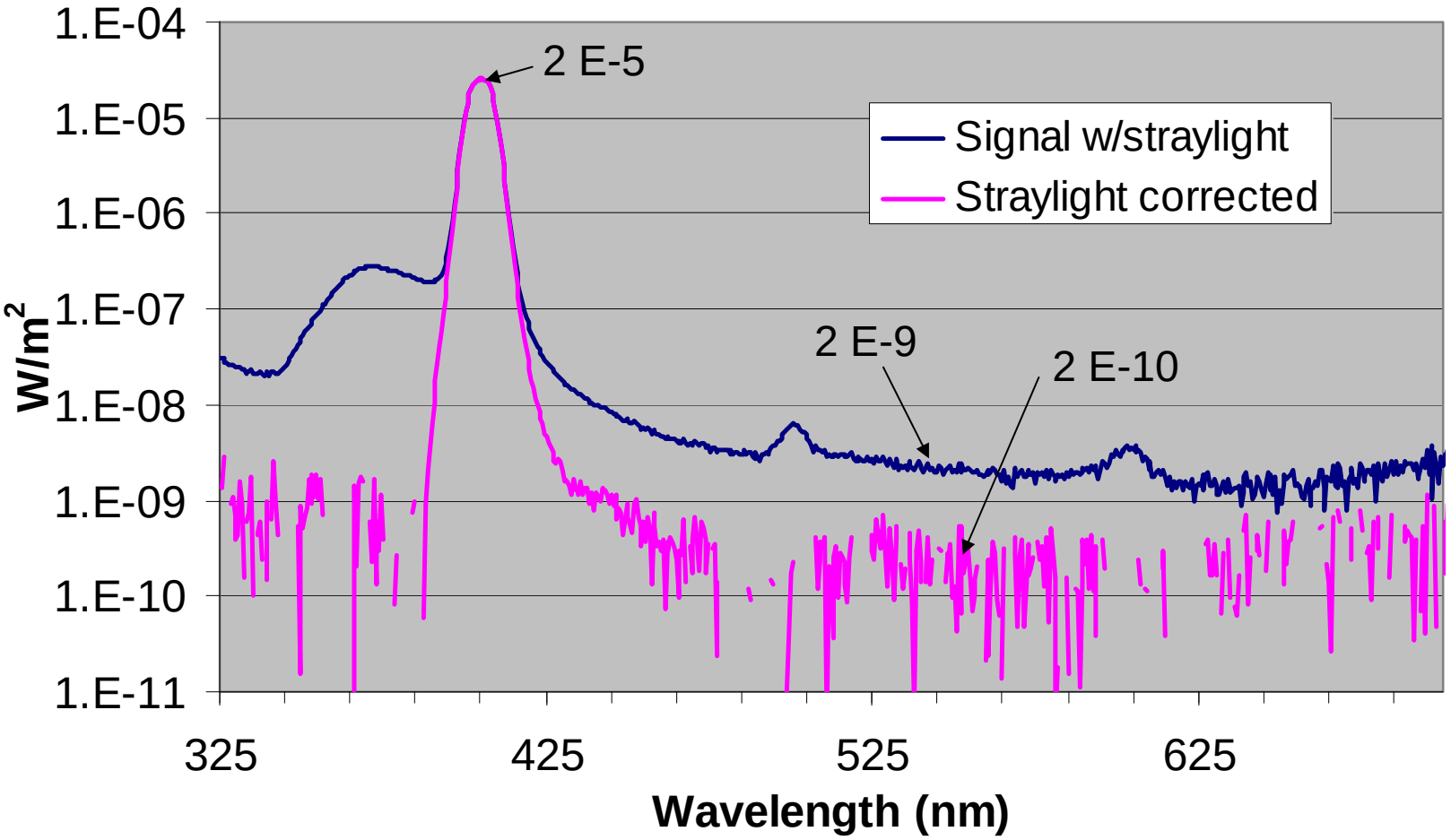
$\Delta F = 0.017$

$R_L^B = 15.23$

$\frac{\partial R_L^B}{\partial F} = -15.48$

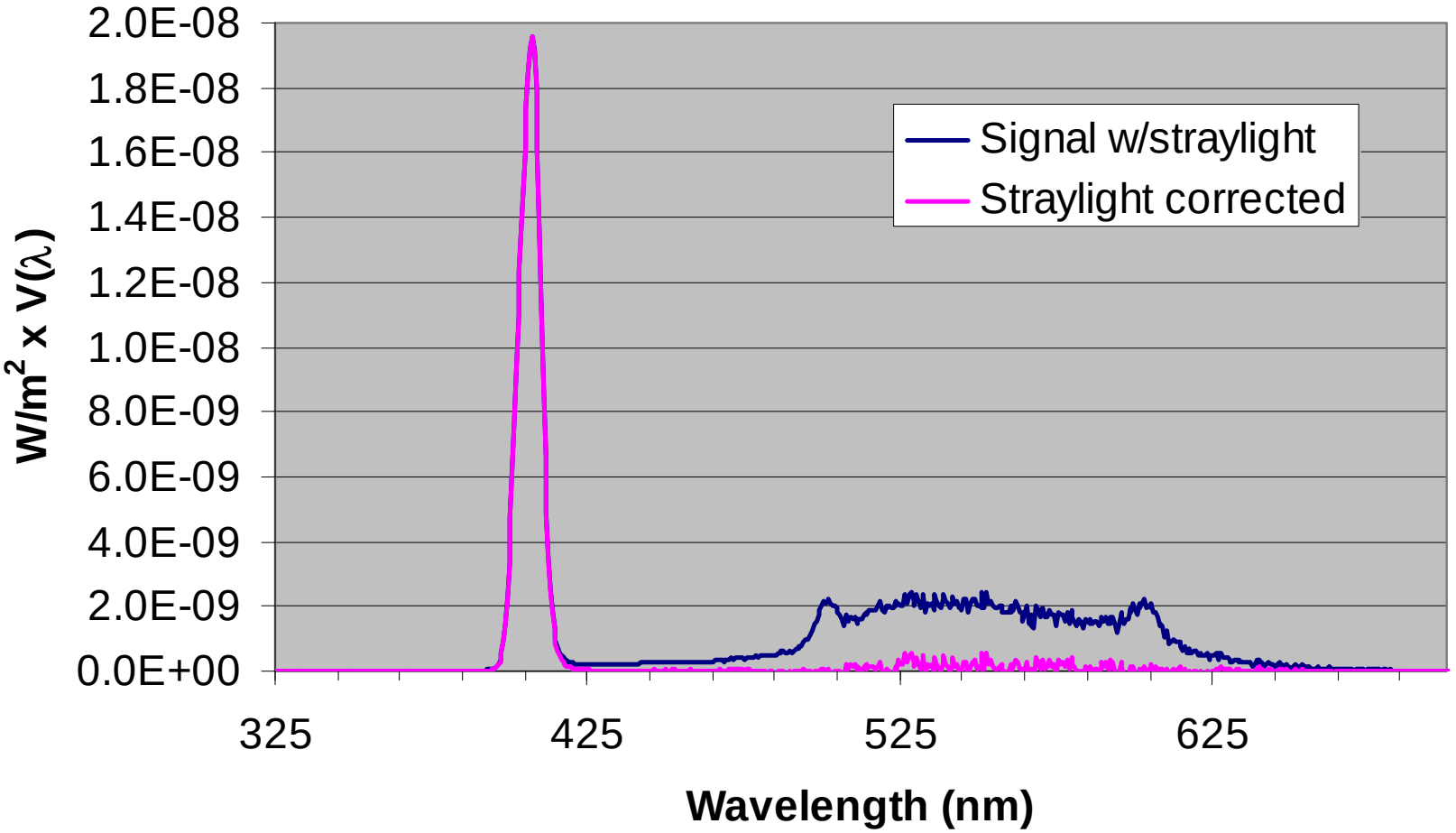
$\frac{\Delta R_L^B}{R_L^B} = 2.4\,\%$

Out-of-band Stray Light - Detector



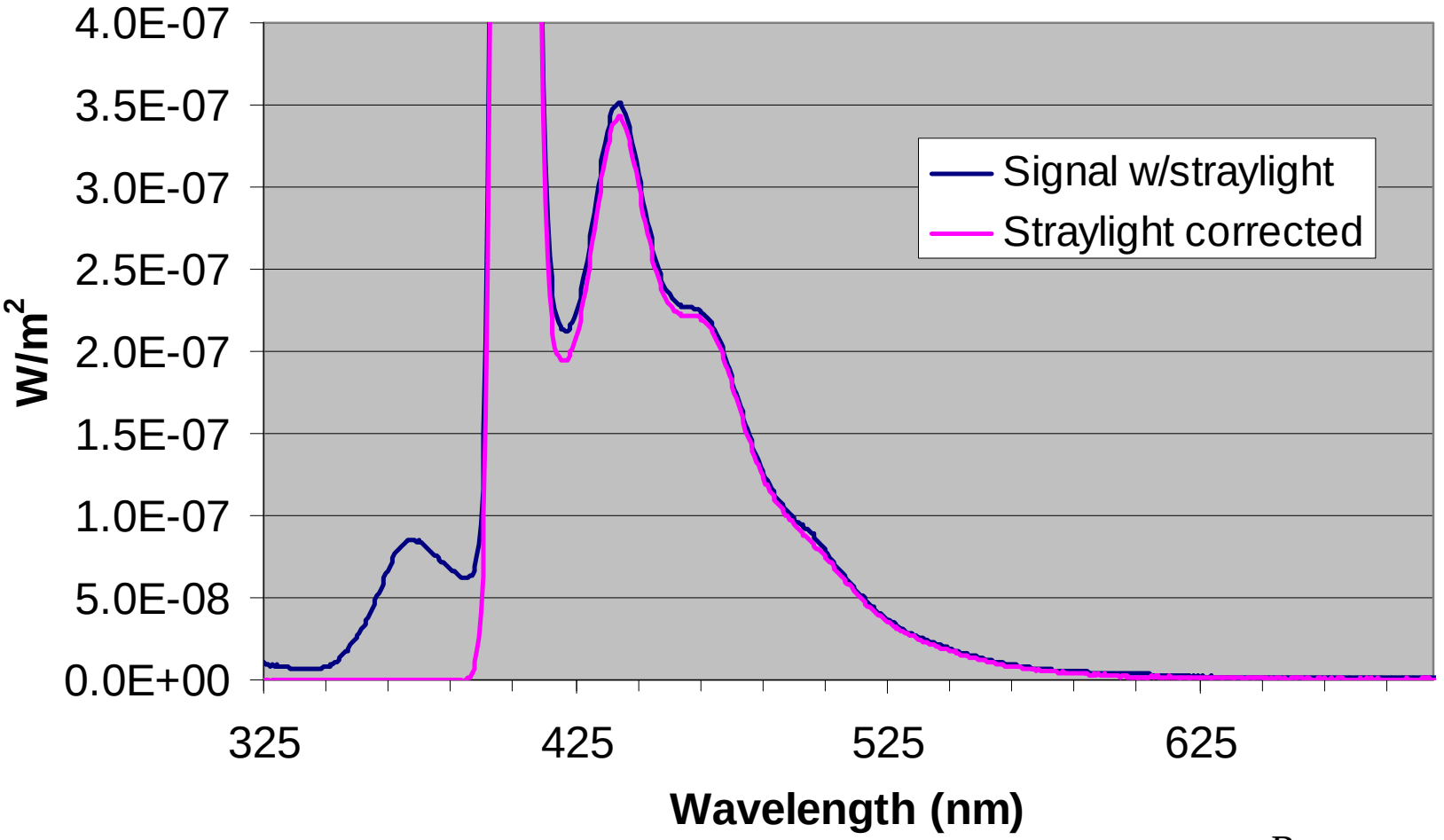
Stray light 0.423 % Corrected 0.036 %

Out-of-band Stray Light - Detector



Straylight $R_L^B = 6.88$ Corrected $R_L^B = 15.23$ 45 %

Out-of-band Stray Light - Detector



$$\frac{\partial R_L^B}{\partial S} = \frac{-511007\%}{\text{Stray Rejection}} \quad \text{at Stray Rejection} = 10^{-5} \qquad \frac{\Delta R_L^B}{R_L^B} = 7.2\,\%$$

Precision Prediction - Filter

Luminance Ratio						
Component	Symbol	Value	ΔX_i	$\partial R_L^B/\partial X_i$	Contribution	%
Sample signal	s	4.212 V	0.04 V	3.62 V^{-1}	0.0209	1.3
Sample dark signal	s_d	0.000 V	0.04 V	-3.62 V^{-1}	0.0209	1.3
Reference signal	s_P	0.3500 V	0.0035 V	-43.52 V^{-1}	0.0232	1.4
Reference dark signal	$s_{P,d}$	0.0000 V	0.0035 V	43.52 V^{-1}	0.0232	1.4
Spectral mismatch C_f sample	F	0.984	2 nm	0.091 nm^{-1}	0.0334	1.7
Spectral mismatch C_f reference	F_P	0.321	2 nm	0.366 nm^{-1}	0.5346	6.8
Standard luminance reflectance	ρ_B	0.97	0.003	15.70	0.0022	0.4
Excitation wavelength	λ_B	1.0	2 nm	-1.52 nm^{-1}	9.2808	28.3
Illumination bandwidth	$\Delta\lambda_B$	1.0	4 nm	0.37 nm^{-1}	2.1383	13.6
Spectral out-of-band light	λ_s	1.0	0.01	-51.91	0.2695	4.8
Linearity of detector	L	1.0	0.01	15.23	0.0232	1.4
Out-of-field sensitivity	O	1.0	0.005	15.23	0.0058	0.7
Voltmeter calibration	c_S	1.0	0.001	15.23	0.0002	0.1
Luminance Ratio	R_L^B	**15.23**	**Predicted precision**		**4.98**	
			Relative precision		**33 %**	