Chemometrics and standardization requirements for both transmission and reflection measurements

Jerry Workman
Unity Scientific/National University

IDRC, July 30, 2018

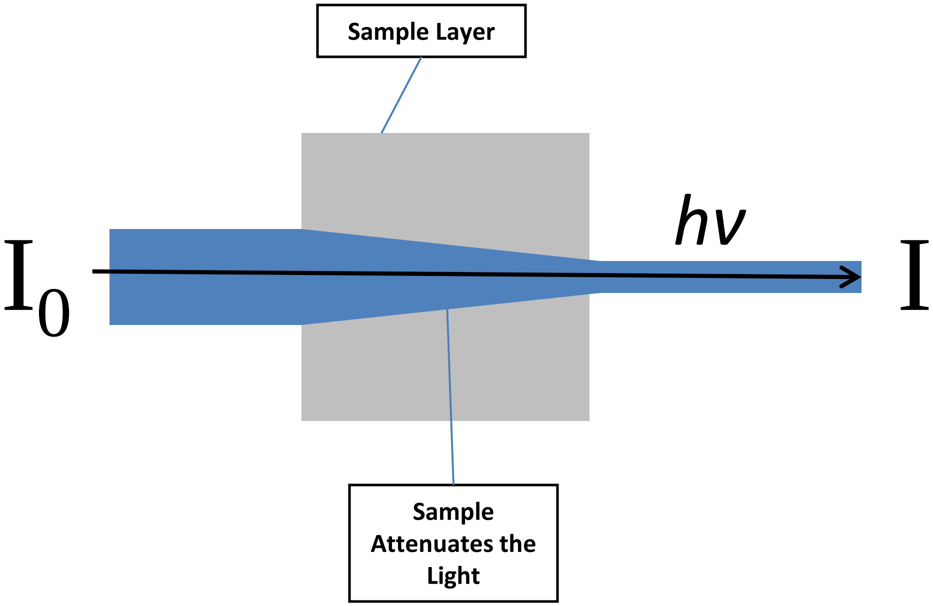
Discussion: What are differences between diffuse reflection and transmission measurements and effects on calibration and calibration transfer?

Why is this important?

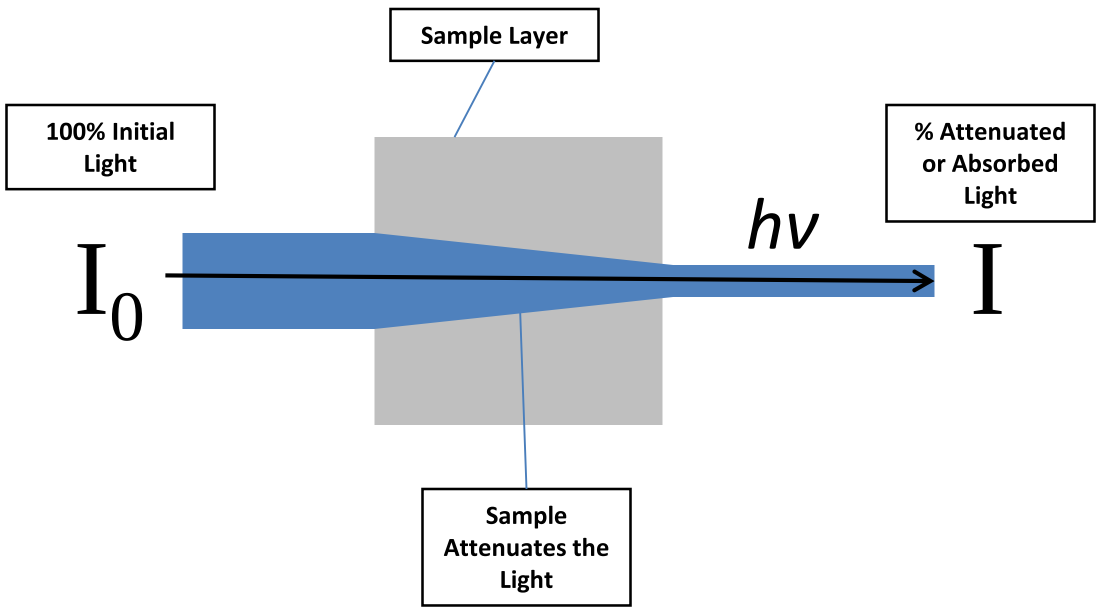
1. Differences between T and DR sample spectra
2. Why is this important?
3. Seamless calibration transfer for quantitative and qualitative applications
4. Database integrity (over time = future-proof)
5. Importance of designing instrumentation that produces identical results (irrespective of design type)
6. Potential for standardizing spectra (future application)
7. Fundamentally sound science (physics based)
8. Basis for regulatory validity

Light Interaction with Matter

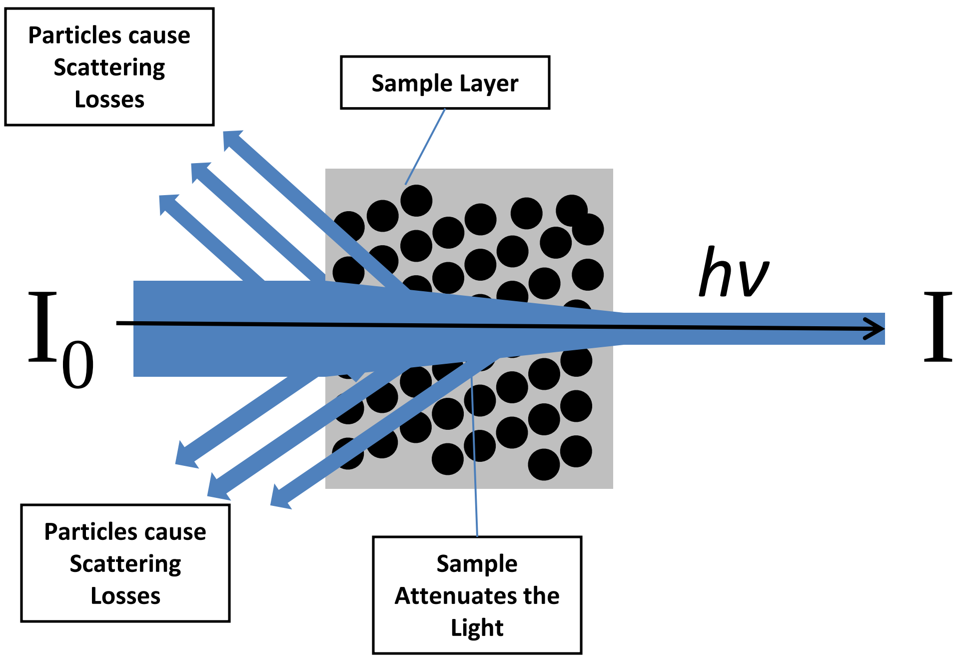
Light Interaction in Transmittance



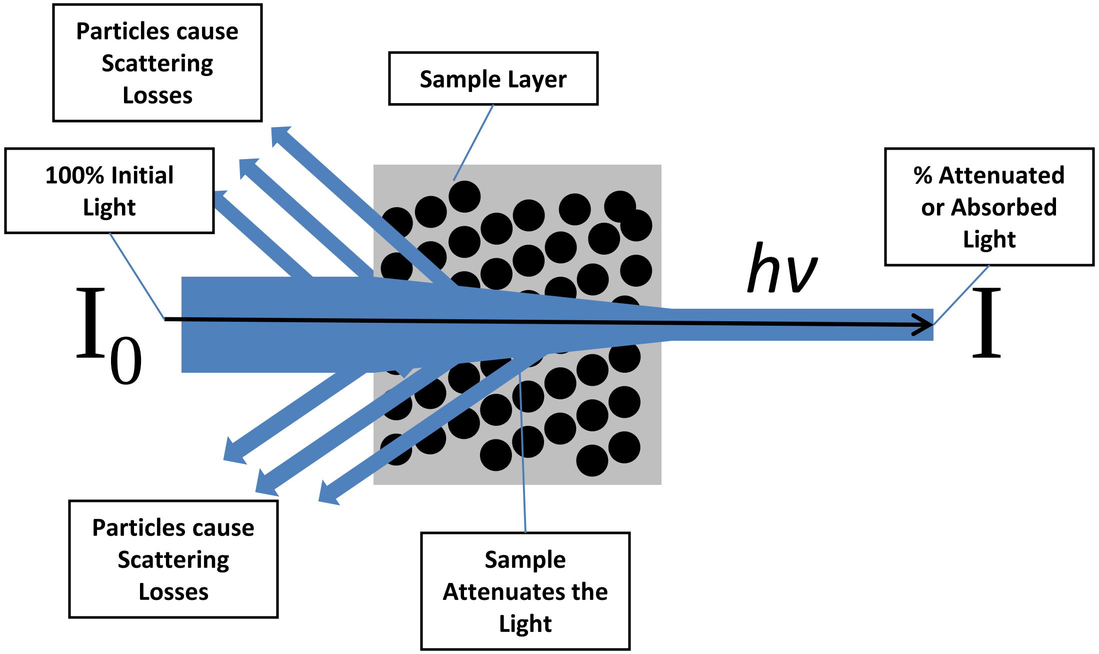
Light Interaction in Transmittance



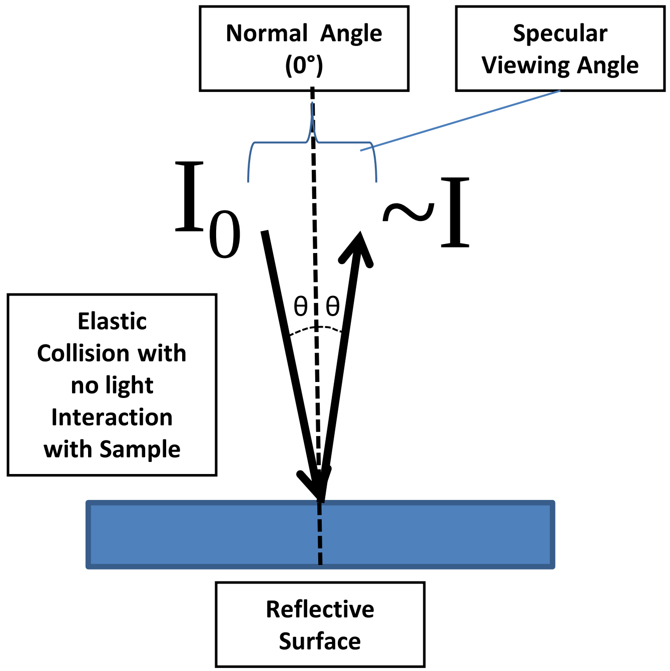
Light Interaction with Particles in Diffuse Transmittance



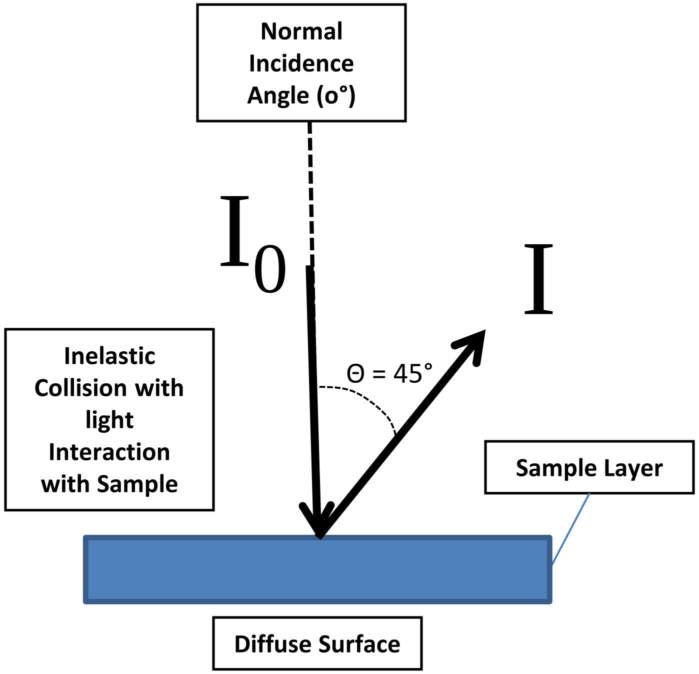
Light Interaction with Particles in Diffuse Transmittance



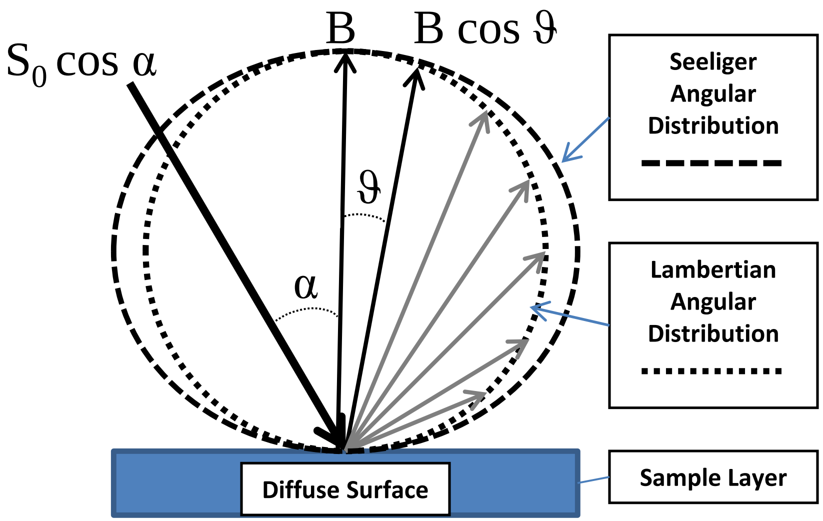
Light as Specular Reflection (Elastic Collision)



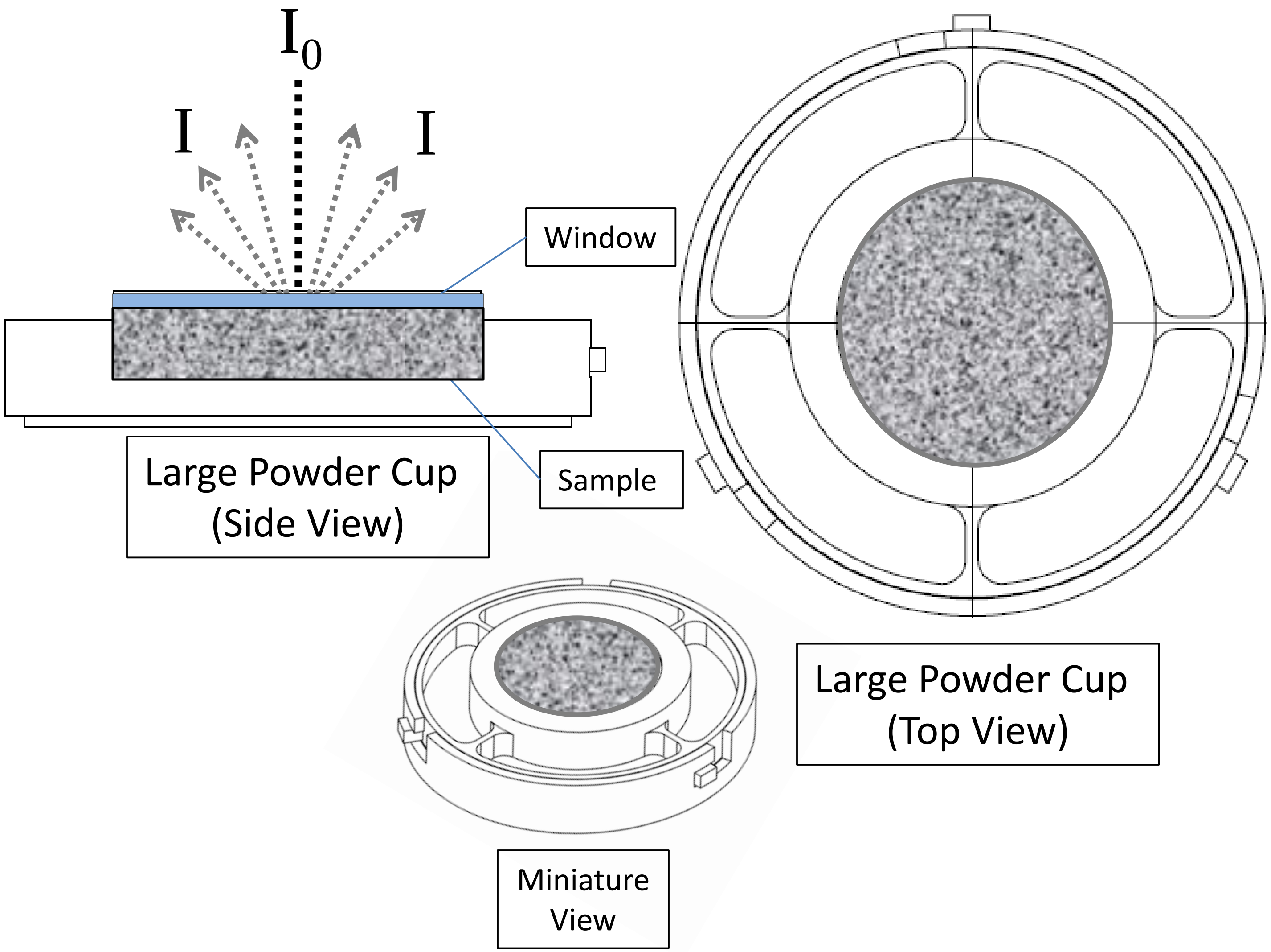
Light as Diffuse Reflection (Inelastic Collision)



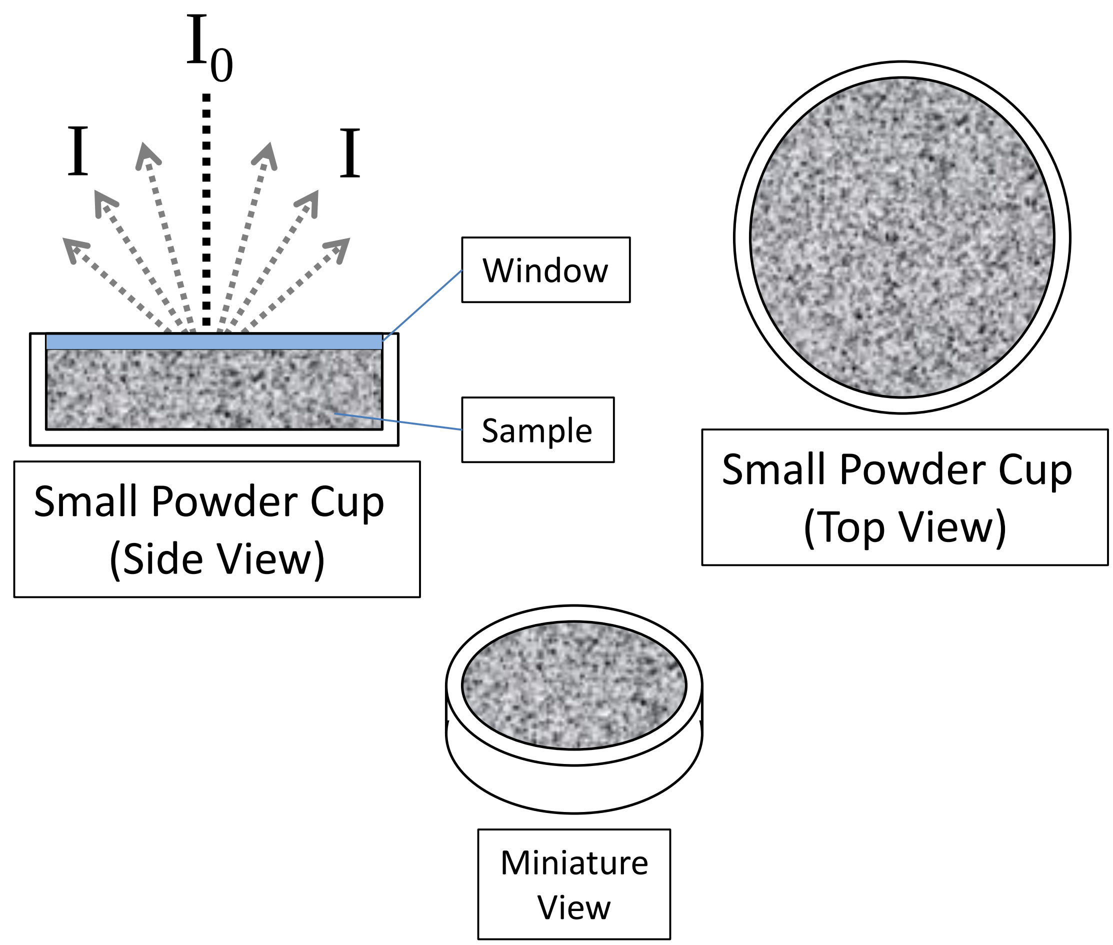
Angular Reflected Energy Distribution

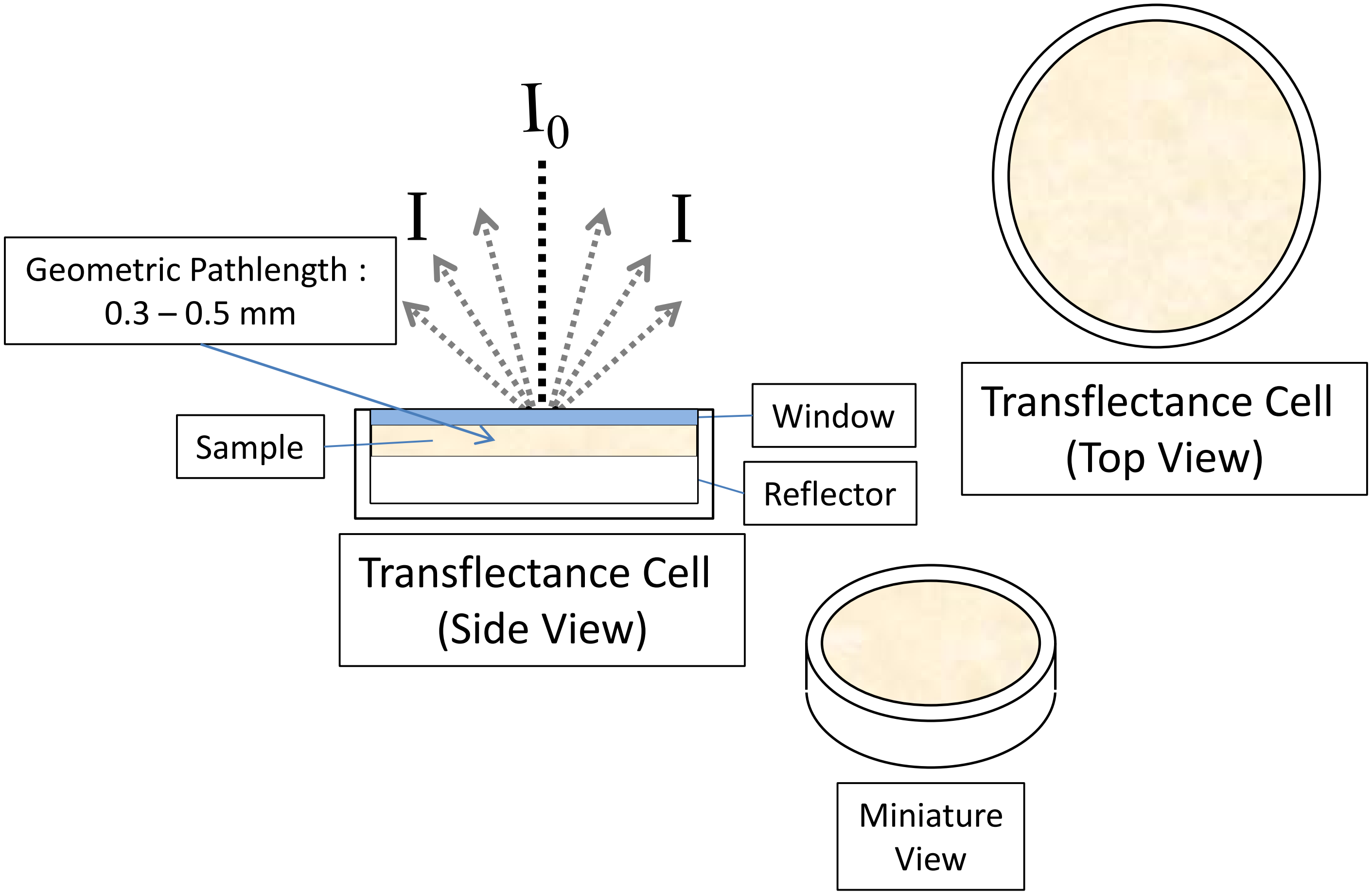


Types of Sampling

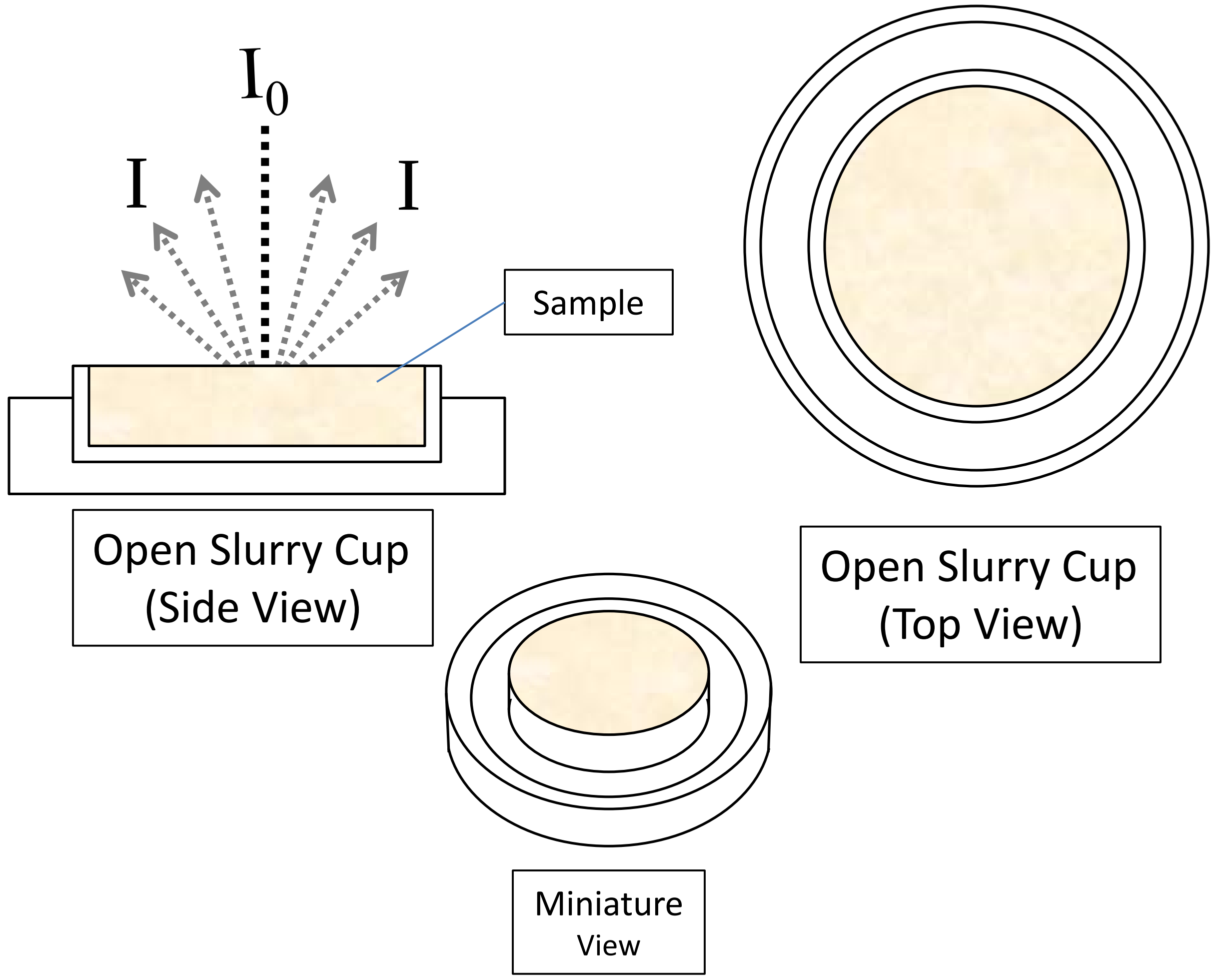


I_0
I
I
Window
Sample
Large Powder Cup (Side View)
Large Powder Cup (Top View)
Miniature View

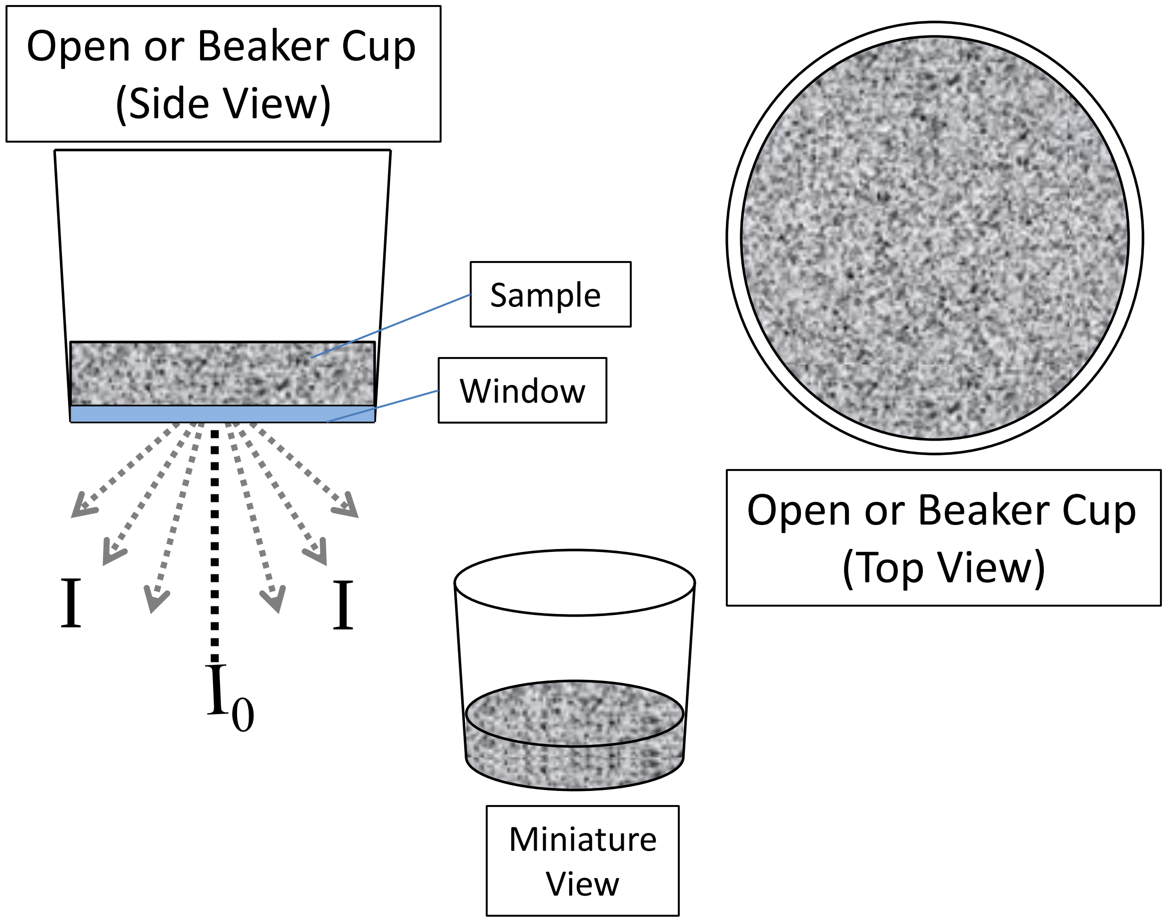

I_0
I
I
Window
Sample
Small Powder Cup
(Side View)
Small Powder Cup
(Top View)
Miniature
View



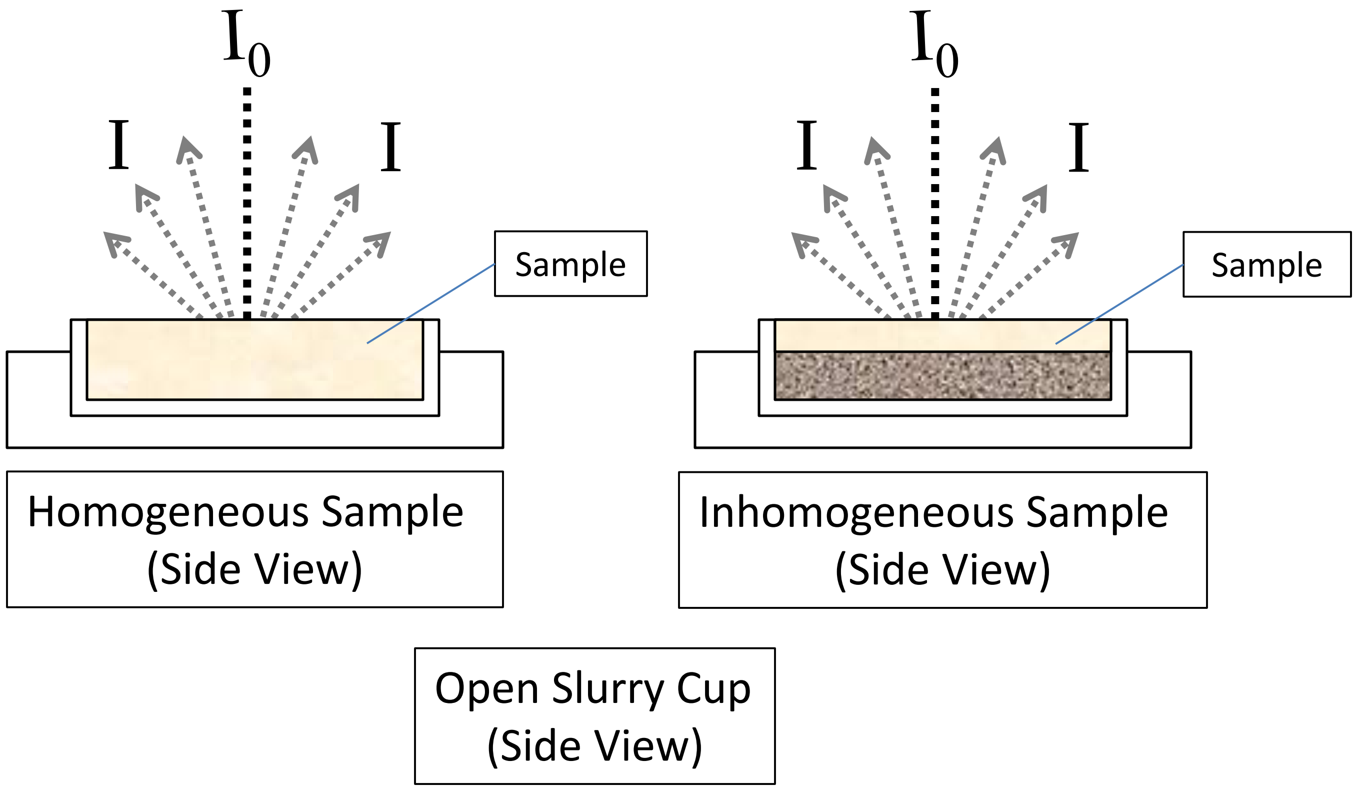
I_0
I
I
Geometric Pathlength : 0.3 – 0.5 mm
Window
Sample
Reflector
Transflectance Cell (Side View)
Transflectance Cell (Top View)
Miniature View



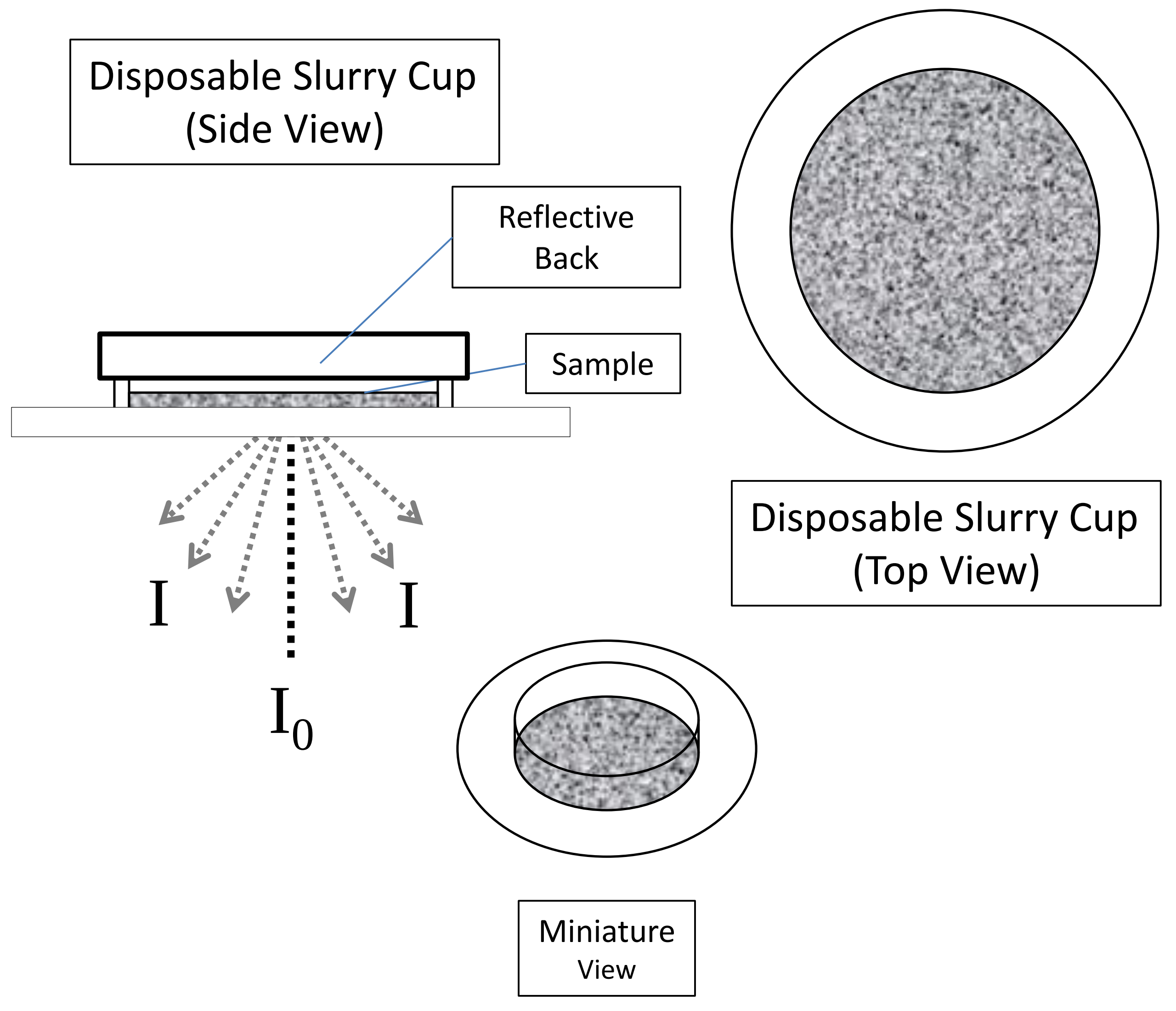
I_0
I
I
Sample
Open Slurry Cup
(Side View)
Open Slurry Cup
(Top View)
Miniature
View

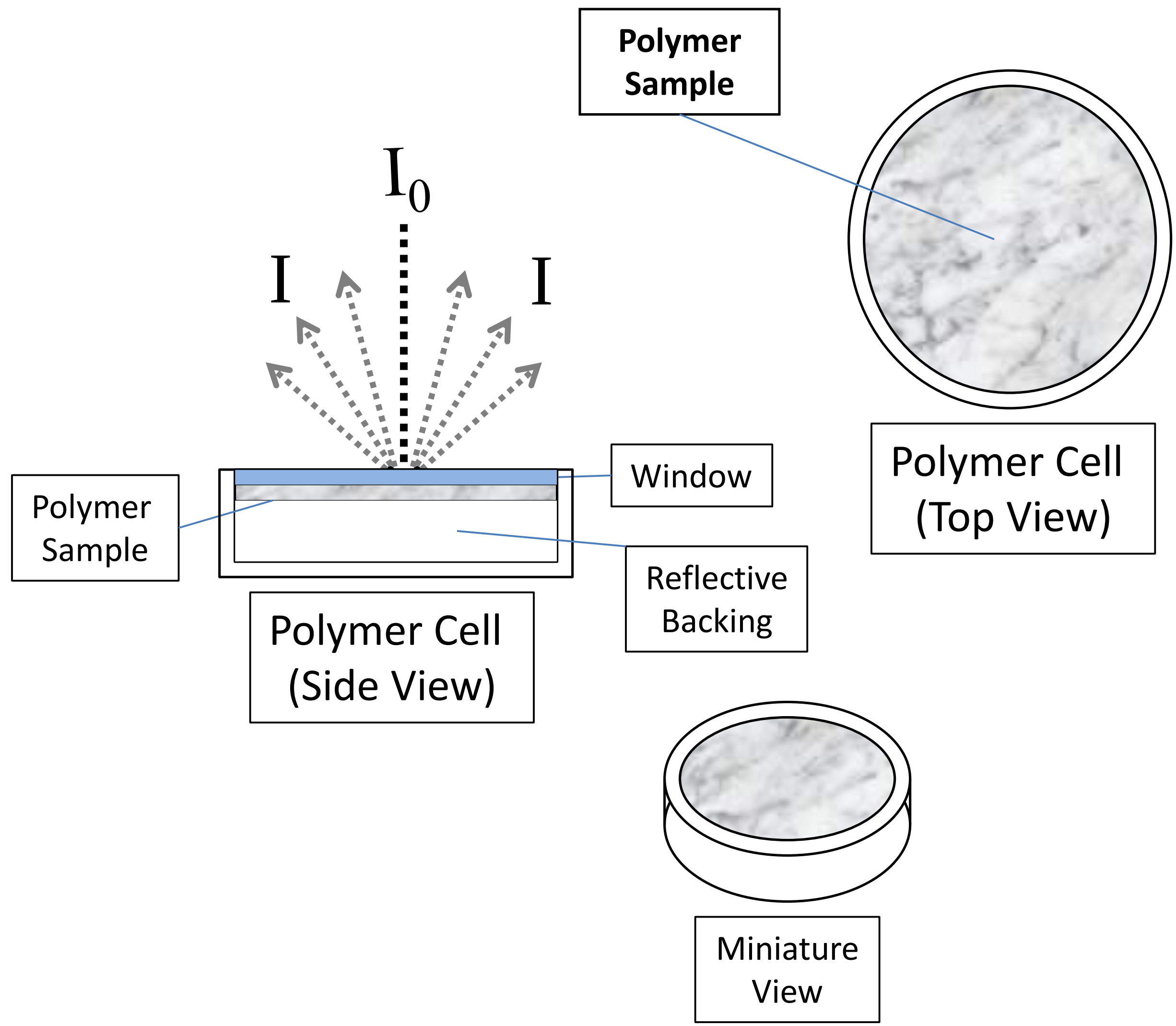


Open or Beaker Cup
(Side View)
Sample
Window
I
I
I0
Open or Beaker Cup
(Top View)
Miniature
View



I_0
I
I
Sample
Homogeneous Sample
(Side View)
I_0
I
I
Sample
Inhomogeneous Sample
(Side View)
Open Slurry Cup
(Side View)

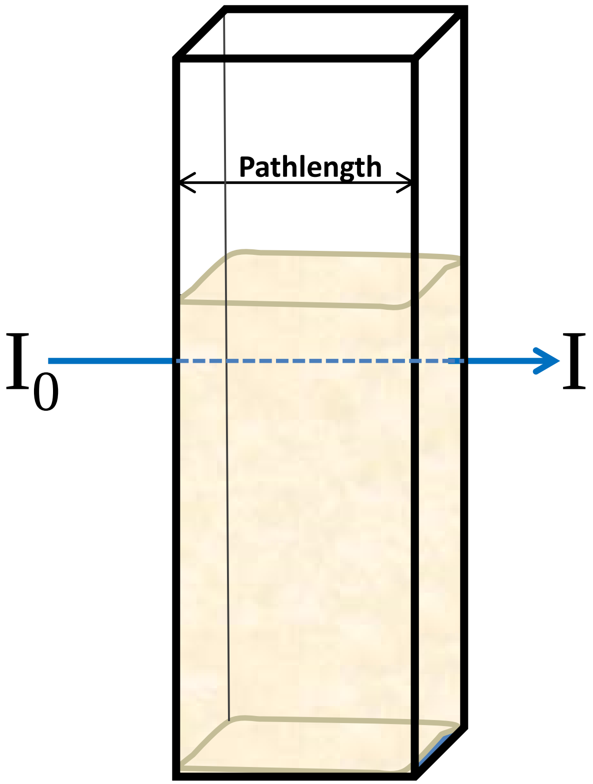

Disposable Slurry Cup
(Side View)
Reflective
Back
Sample
I
I
I0
Disposable Slurry Cup
(Top View)
Miniature
View



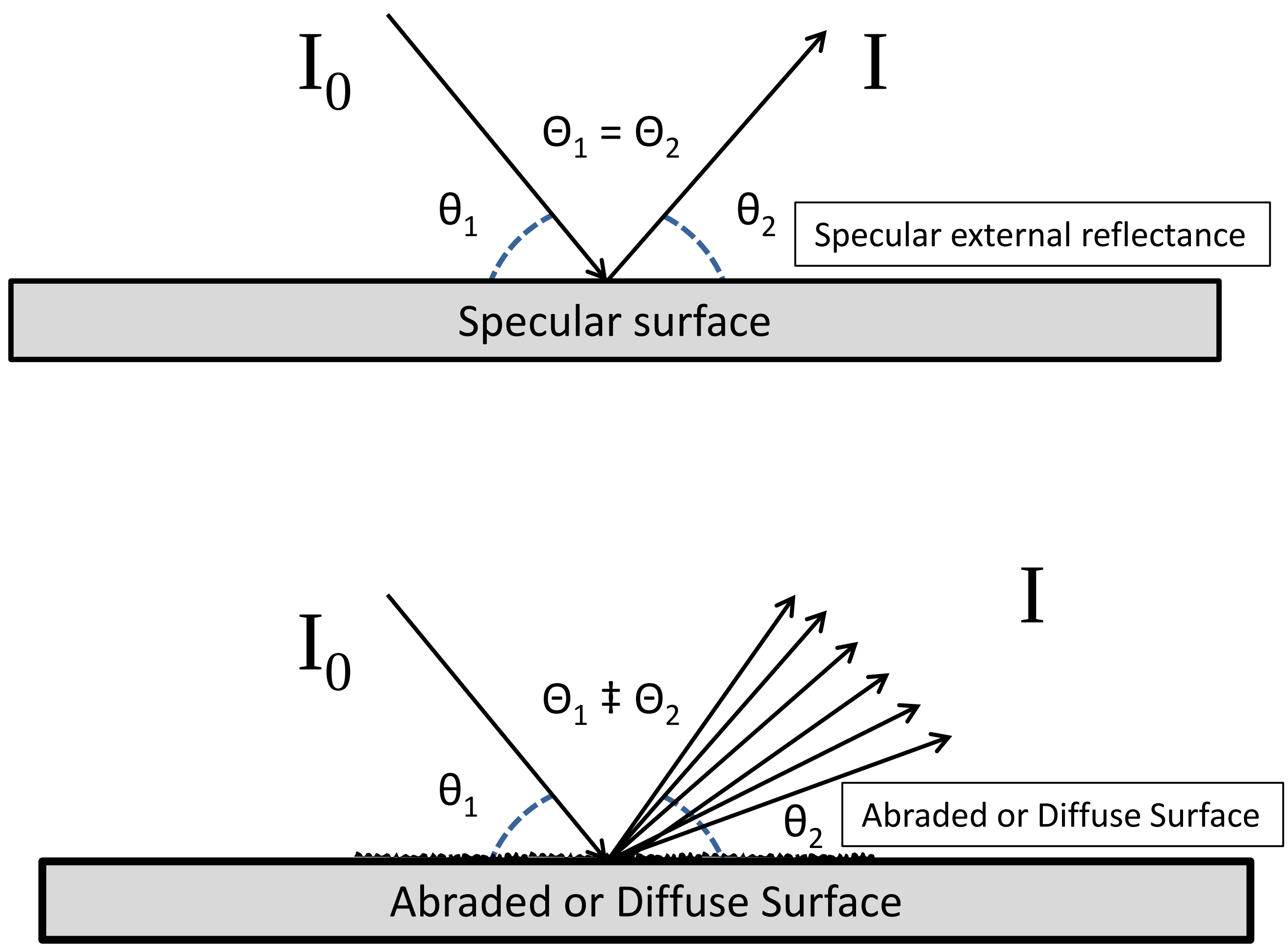
Polymer Sample
I
I_0
I
Polymer Cell (Top View)
Window
Polymer Sample
Reflective Backing
Polymer Cell (Side View)
Miniature View

Liquid cuvet cell types

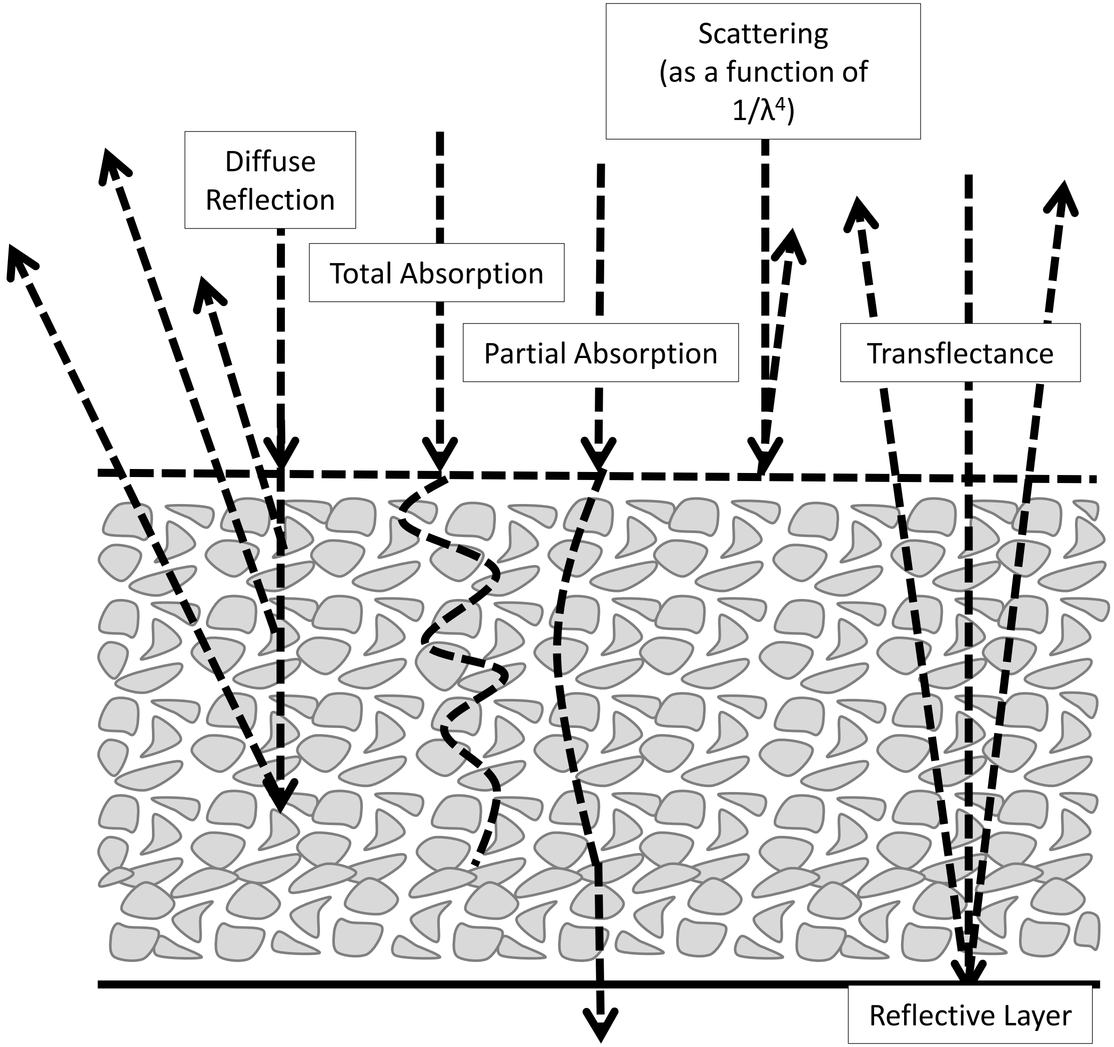
Pathlength is physical distance where light passes through



Rectangular Cuvette



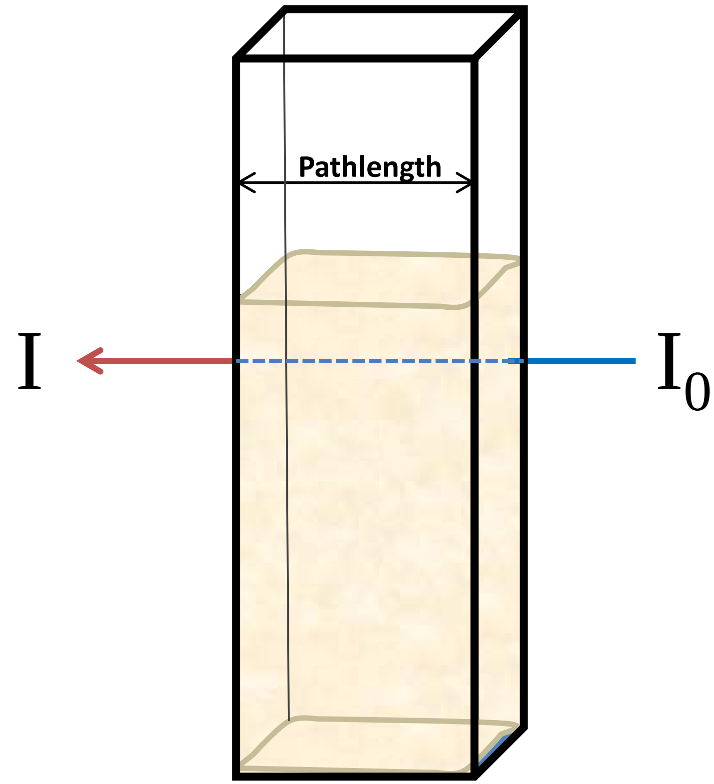
I0
I
Θ1 = Θ2
θ1
θ2
Specular external reflectance
Specular surface
I0
I
Θ1 ‡ Θ2
θ1
θ2
Abraded or Diffuse Surface
Abraded or Diffuse Surface



Scattering
(as a function of
1/λ⁴)
Diffuse
Reflection
Total Absorption
Partial Absorption
Transflectance
Reflective Layer

Transmission

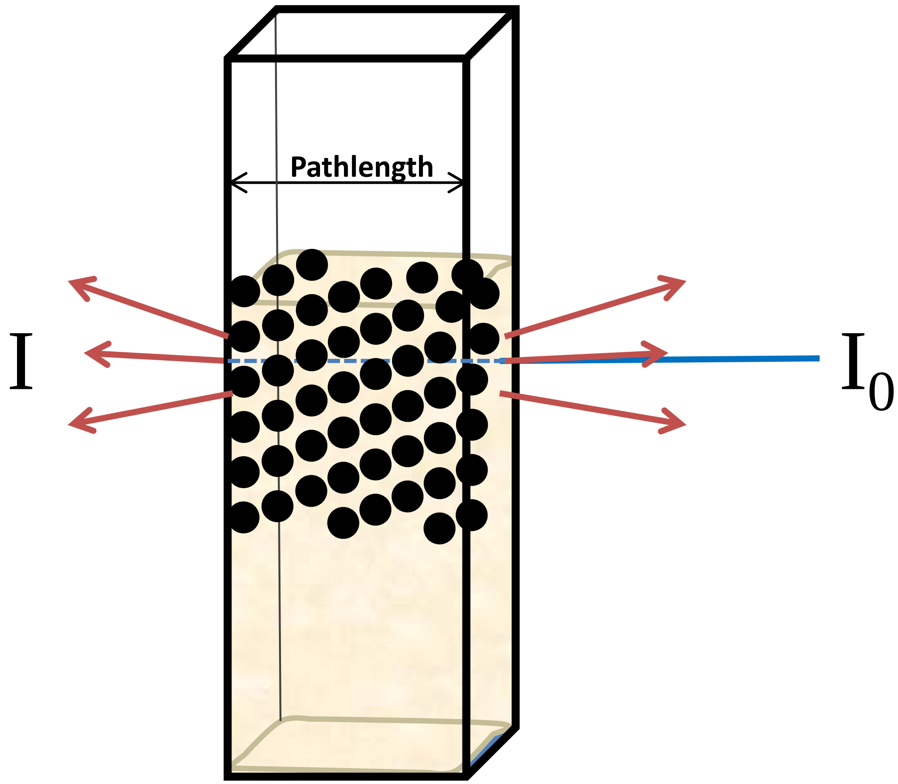
Pathlength is physical distance where light passes through



Rectangular Cuvette

Diffuse Transmission

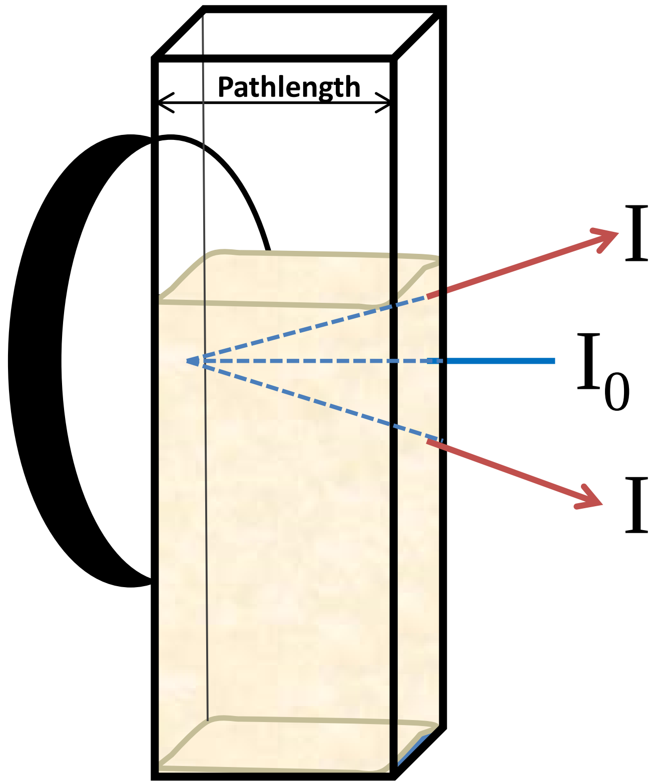
Pathlength is physical distance where light passes through



Rectangular Cuvette

Diffuse Reflection

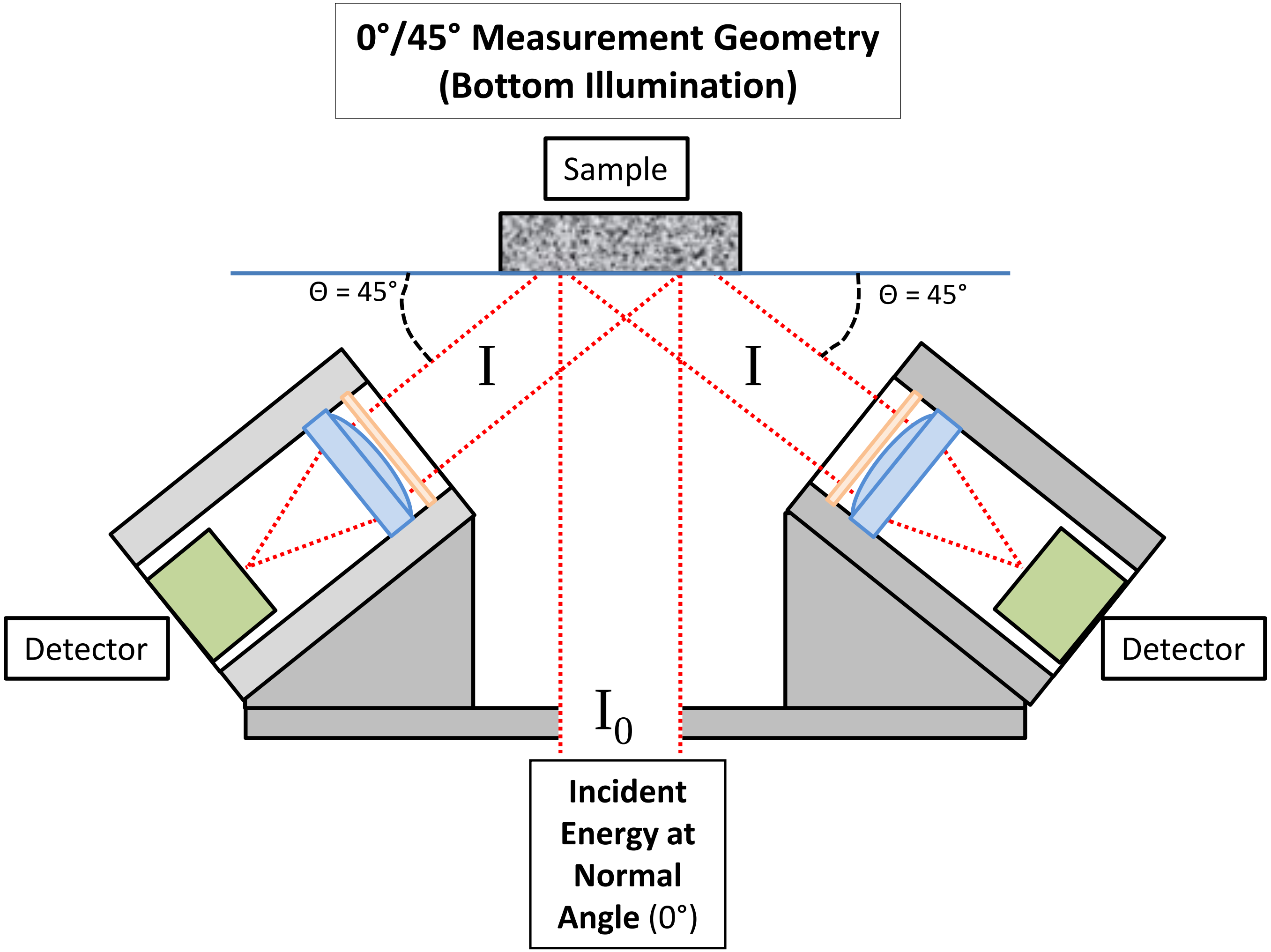
Pathlength is physical distance where light passes through



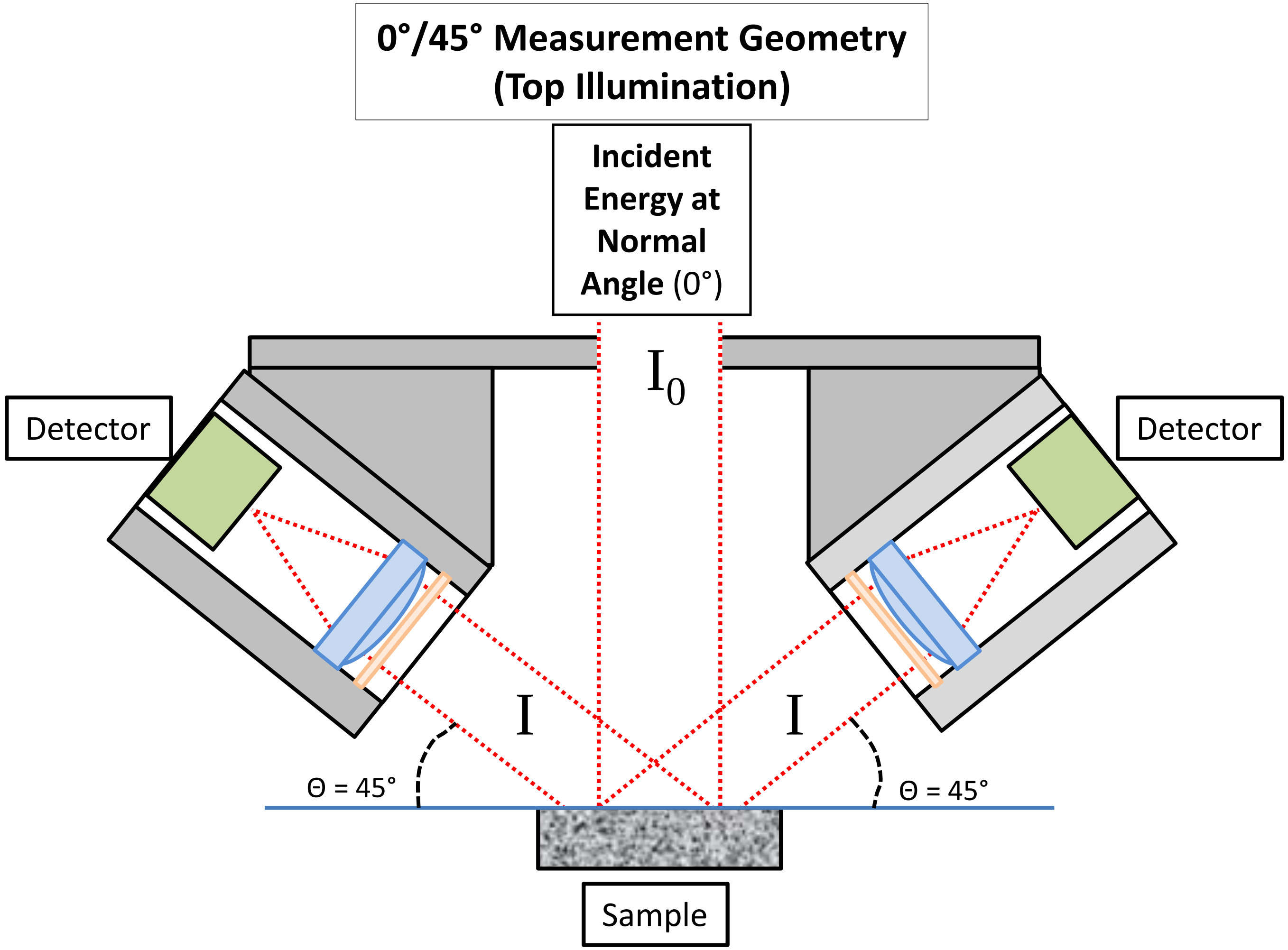
Reflector

Rectangular Cuvette

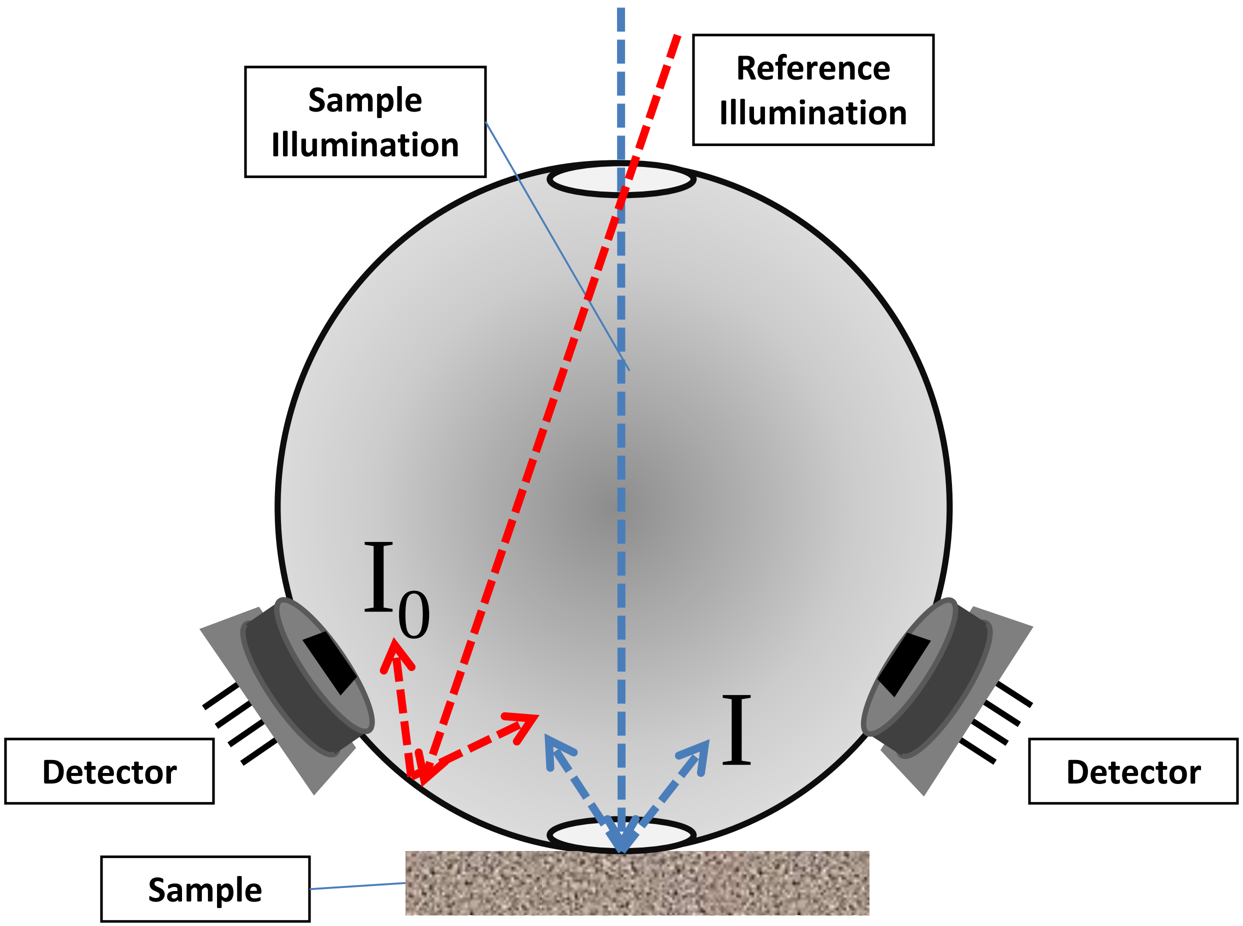
Post-dispersive



Post-dispersive

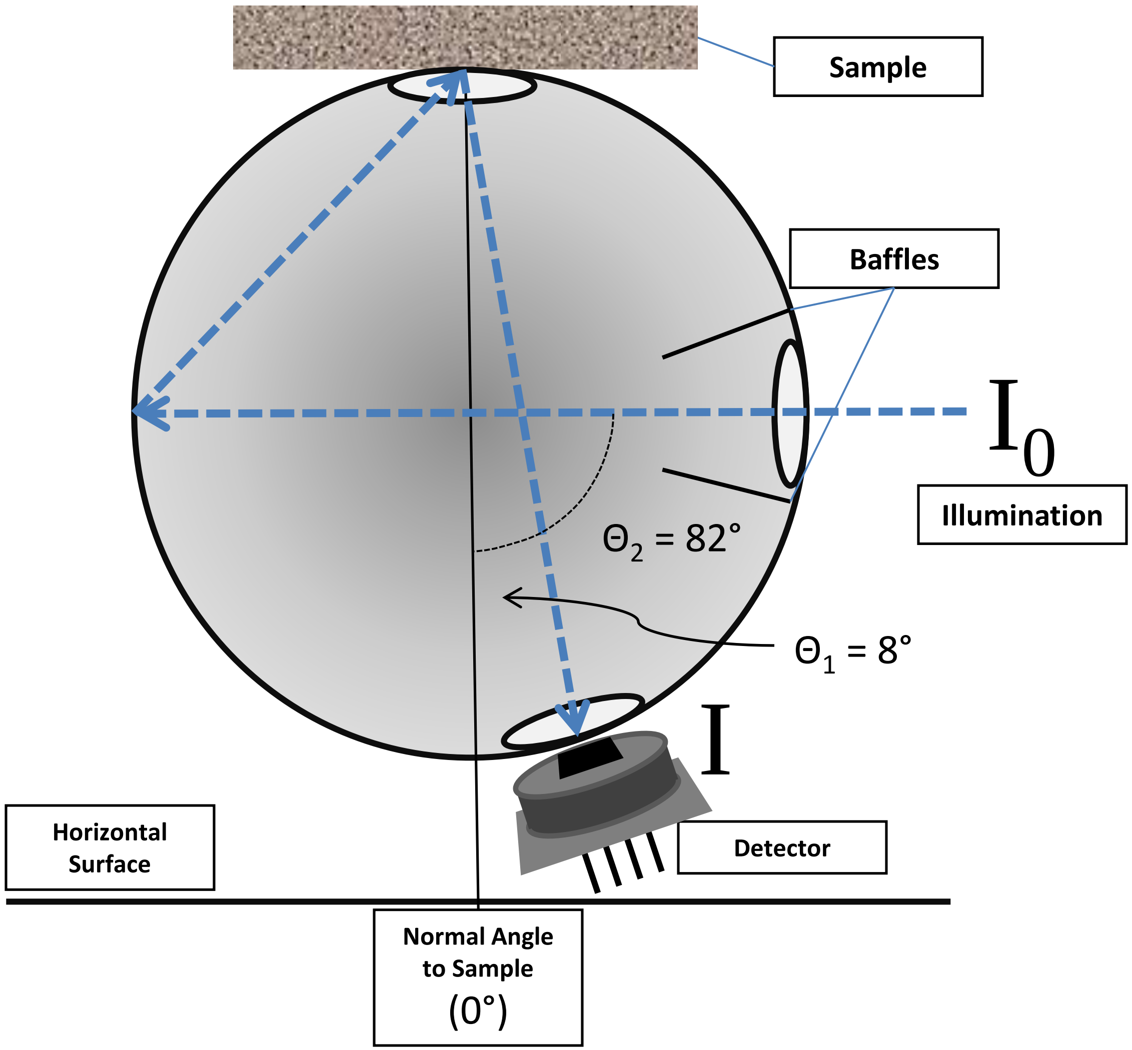


Post-dispersive



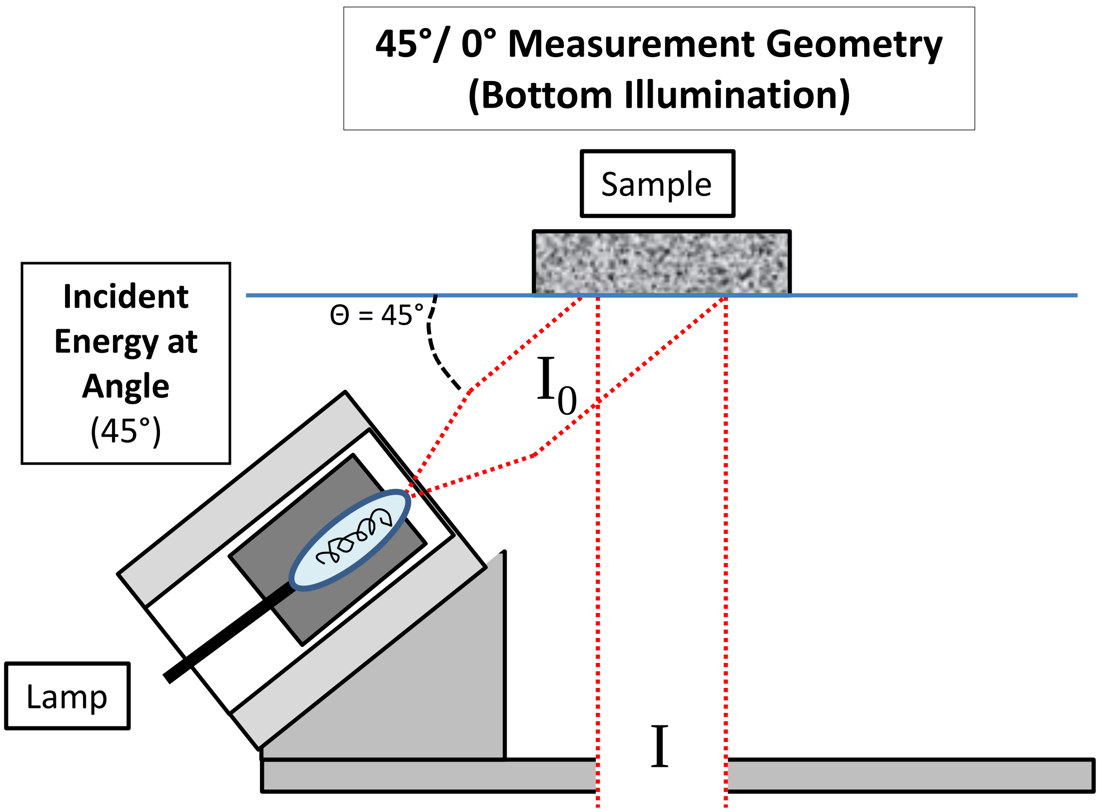
DR Measurement Geometry

Post-dispersive

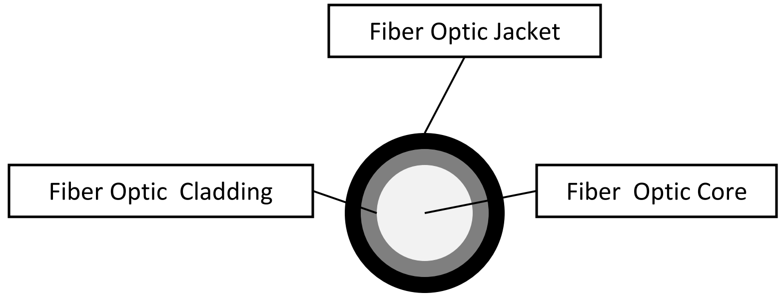


d/8° Measurement Geometry

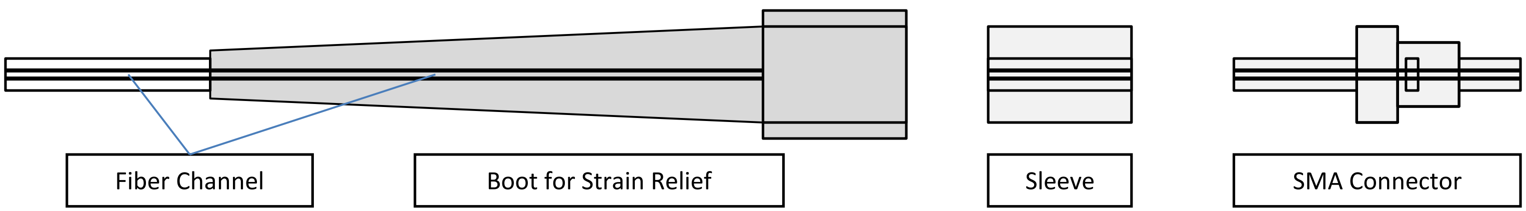
Pre-dispersive



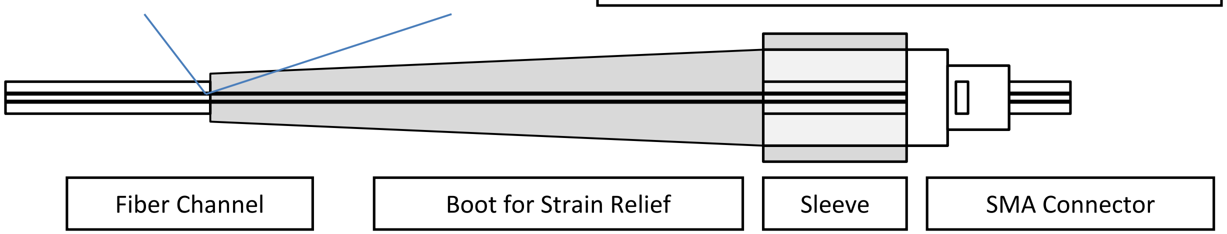
Fiber Optics



Fiber Optic (Cross-Section)



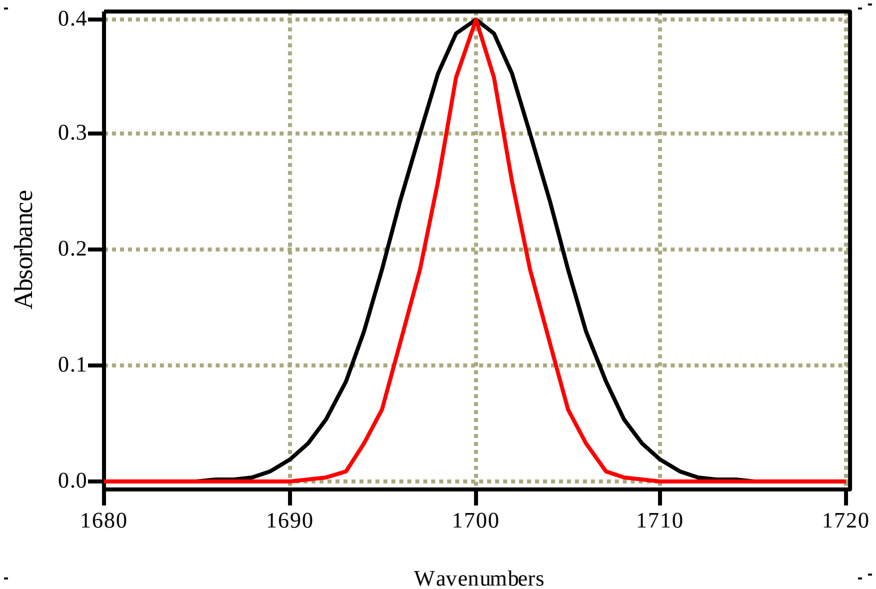
Fiber Optic Connector (Components Cross-Section)

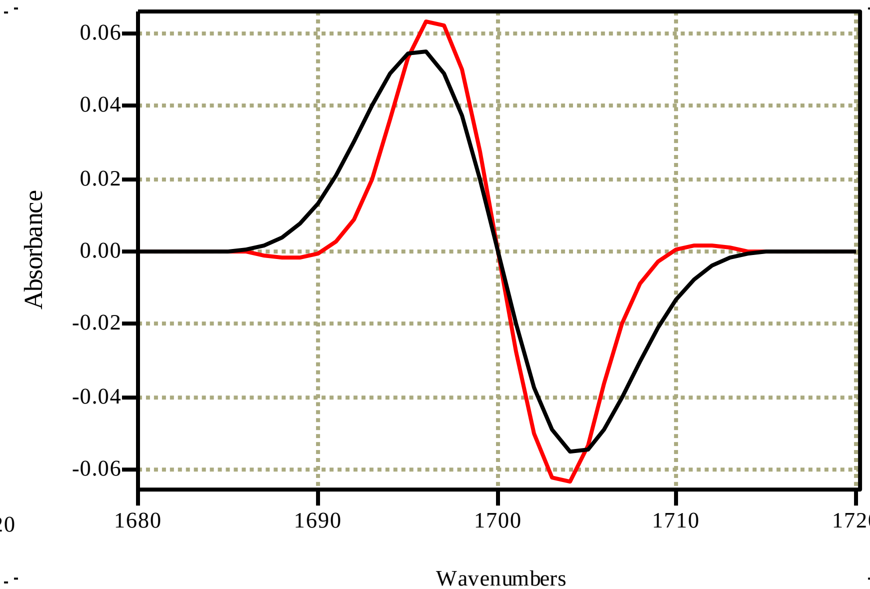


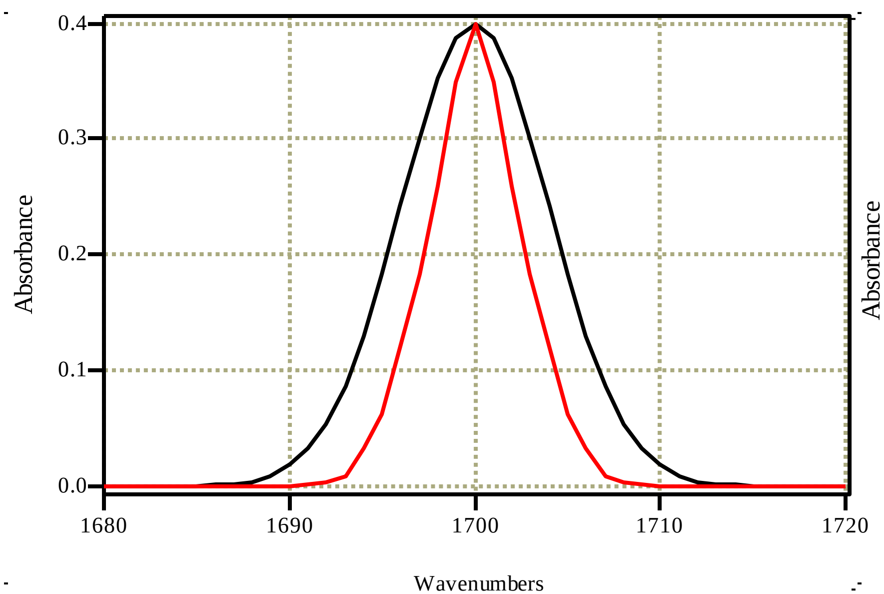
Fiber Optic Connector (Assembled Cross-Section)

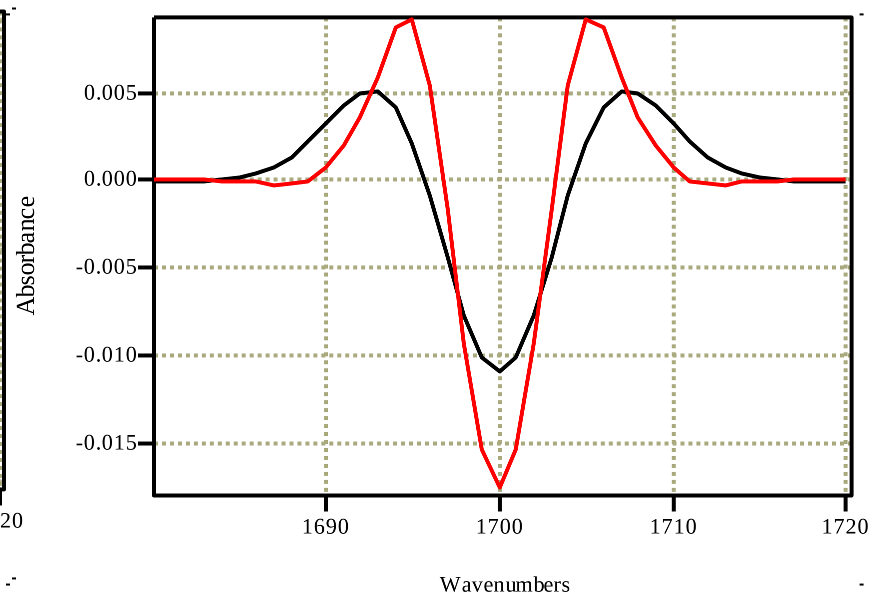
Linewidth/Line Shape differences shown using derivatives

Derivatives vs Resolution and Line Shape

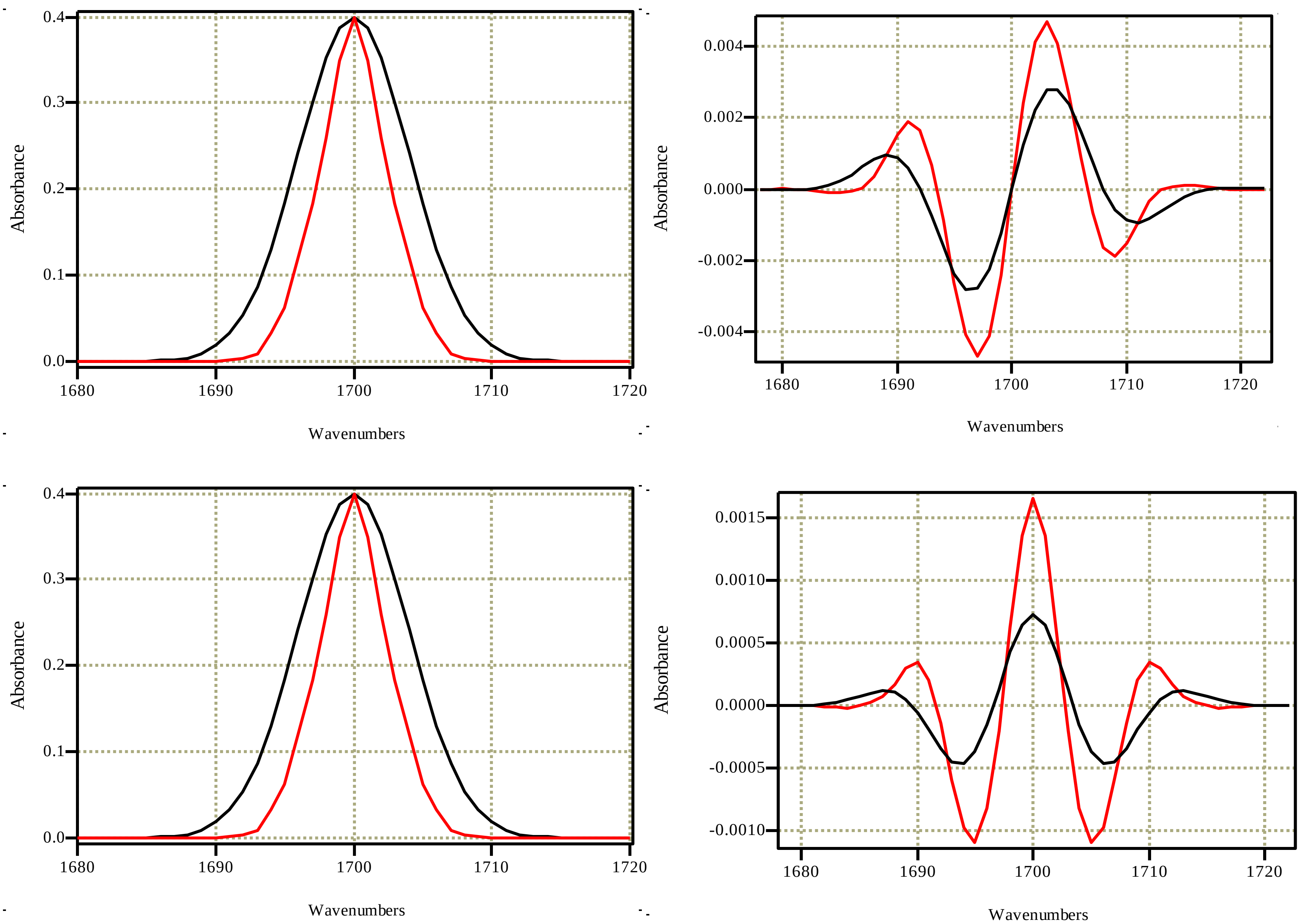




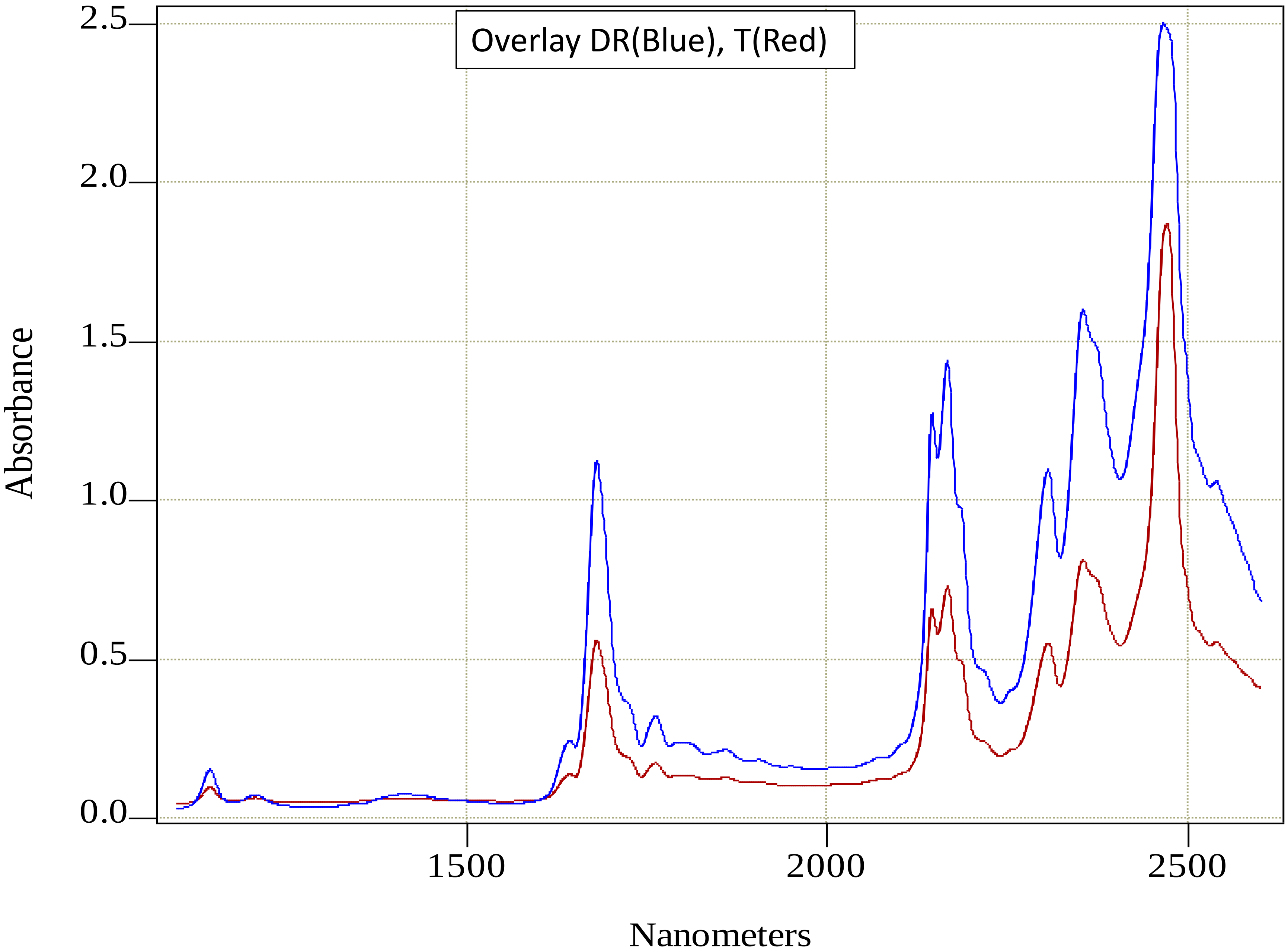




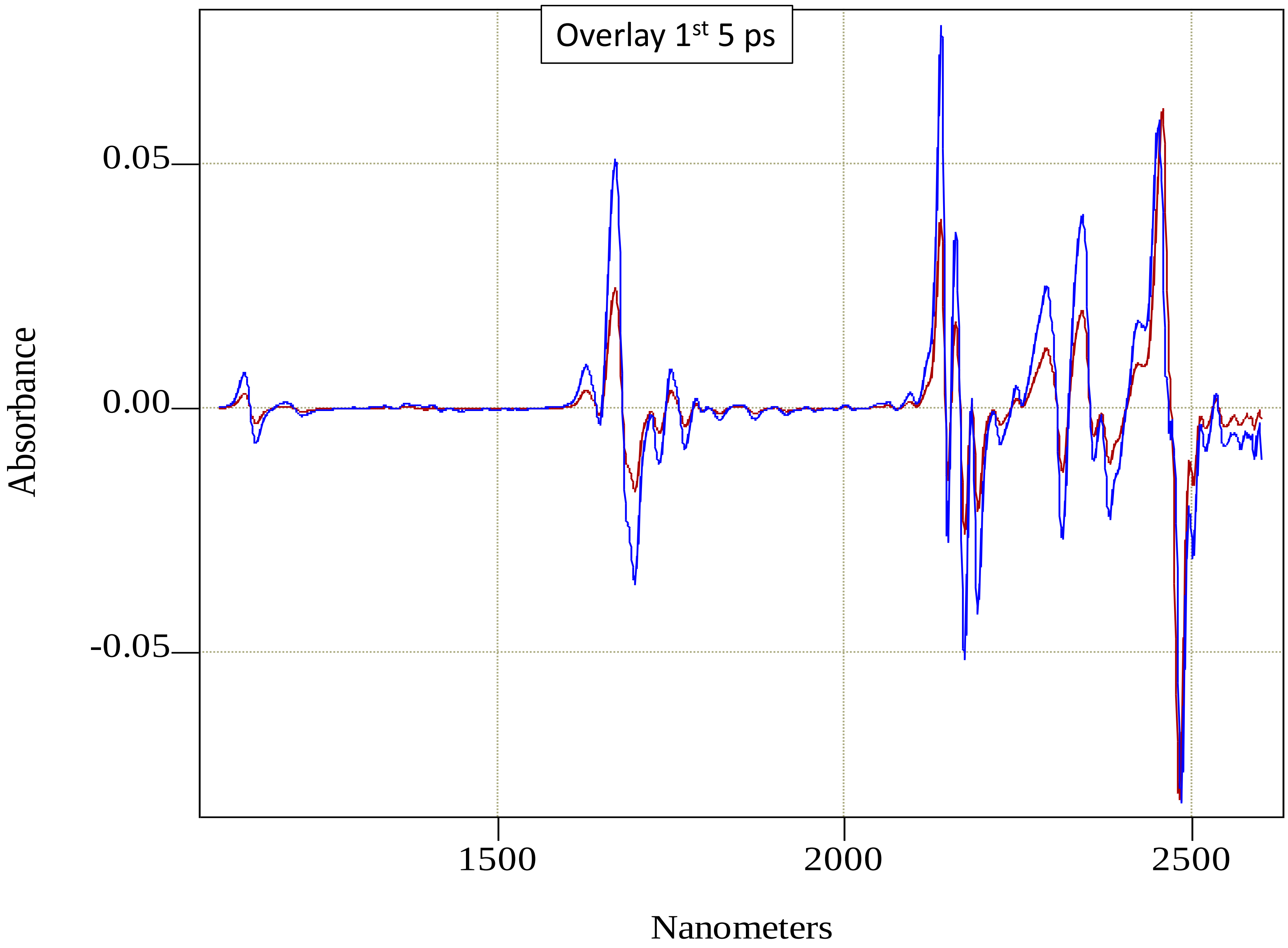
Derivatives vs Resolution and Line Shape



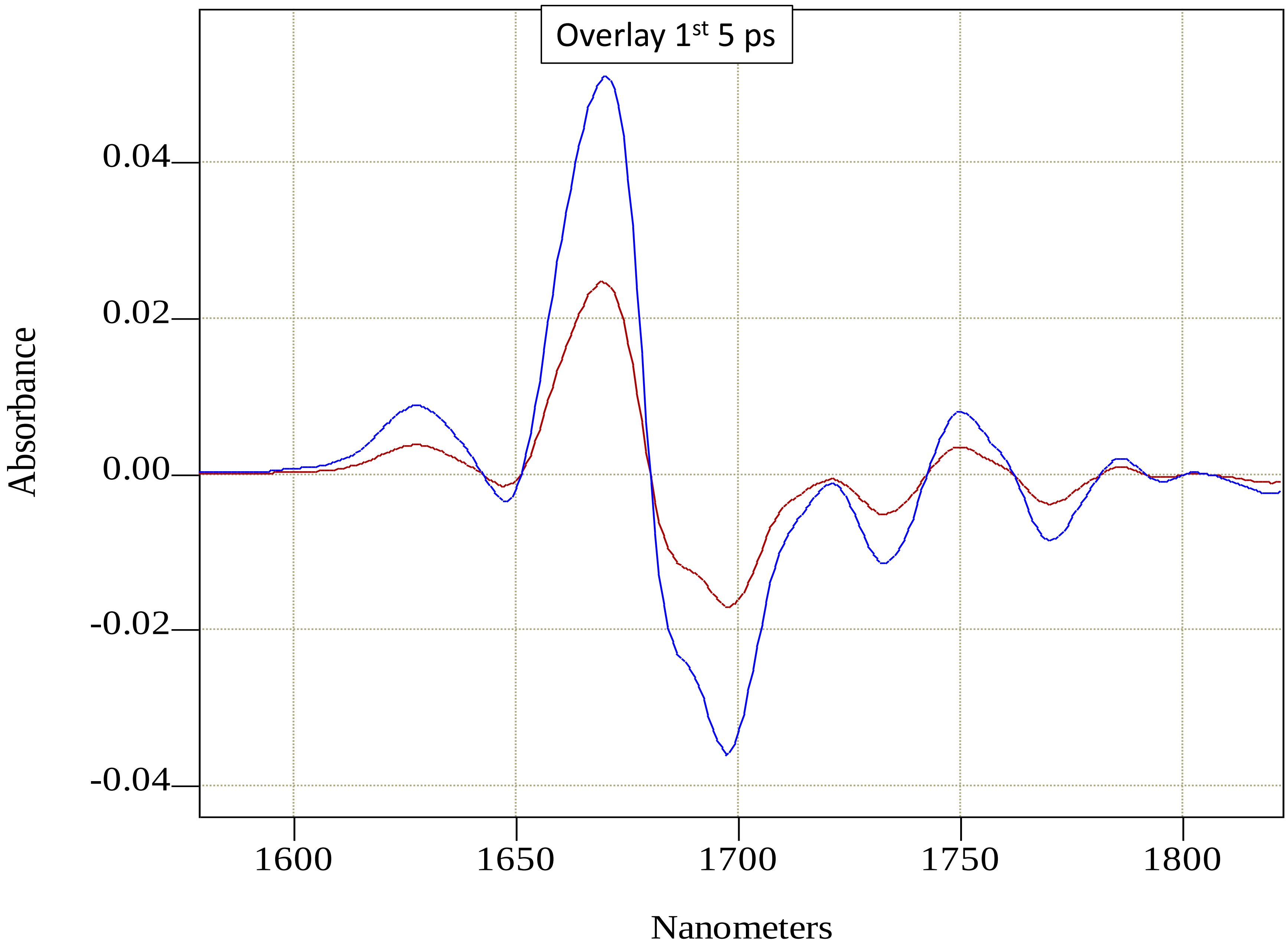
Comparing Transmission and Reflection Spectra: Polystyrene

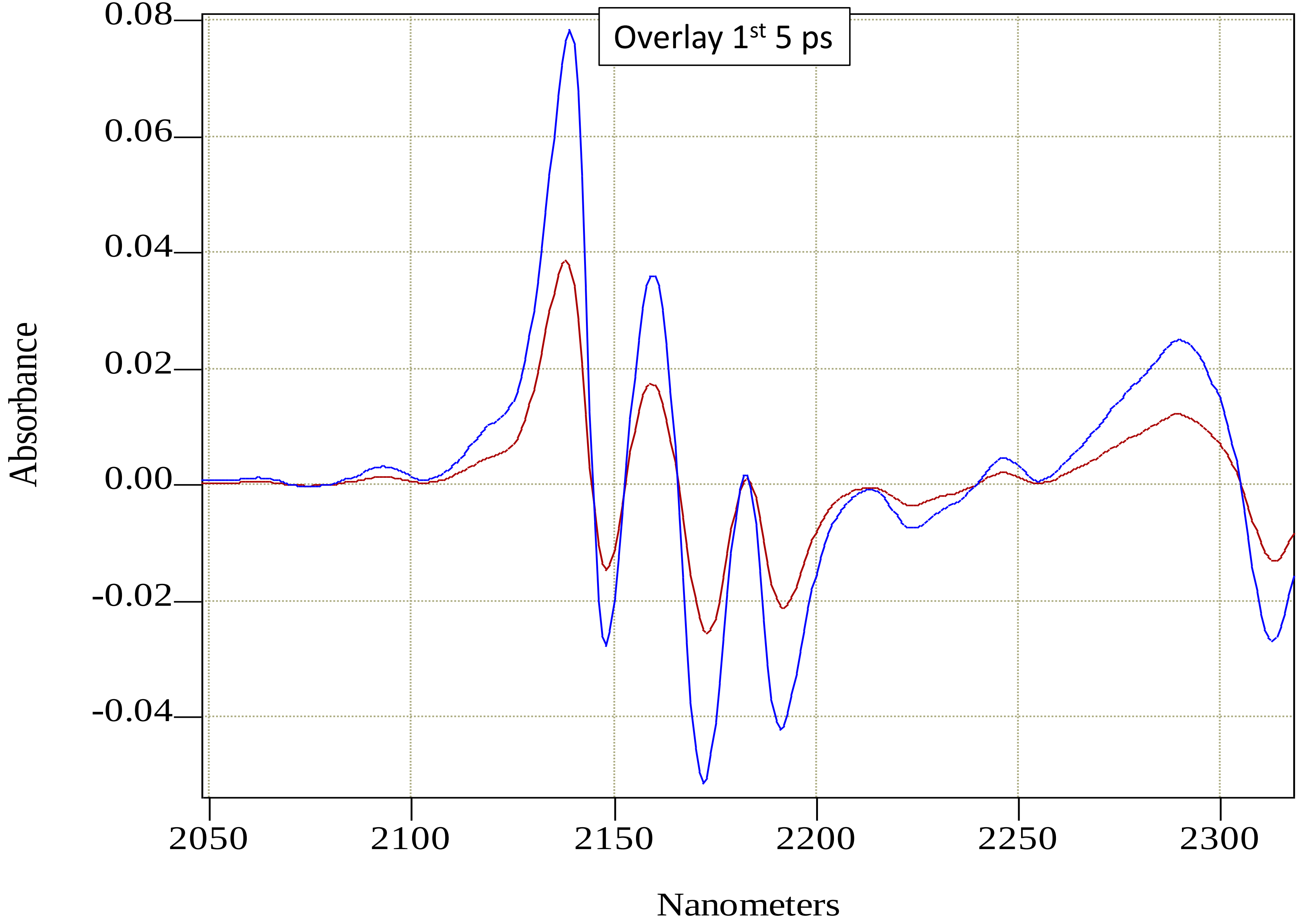


Overlay DR(Blue), T(Red)
2.5
2.0
1.5
1.0
0.5
0.0
Absorbance
1500
2000
2500
Nanometers



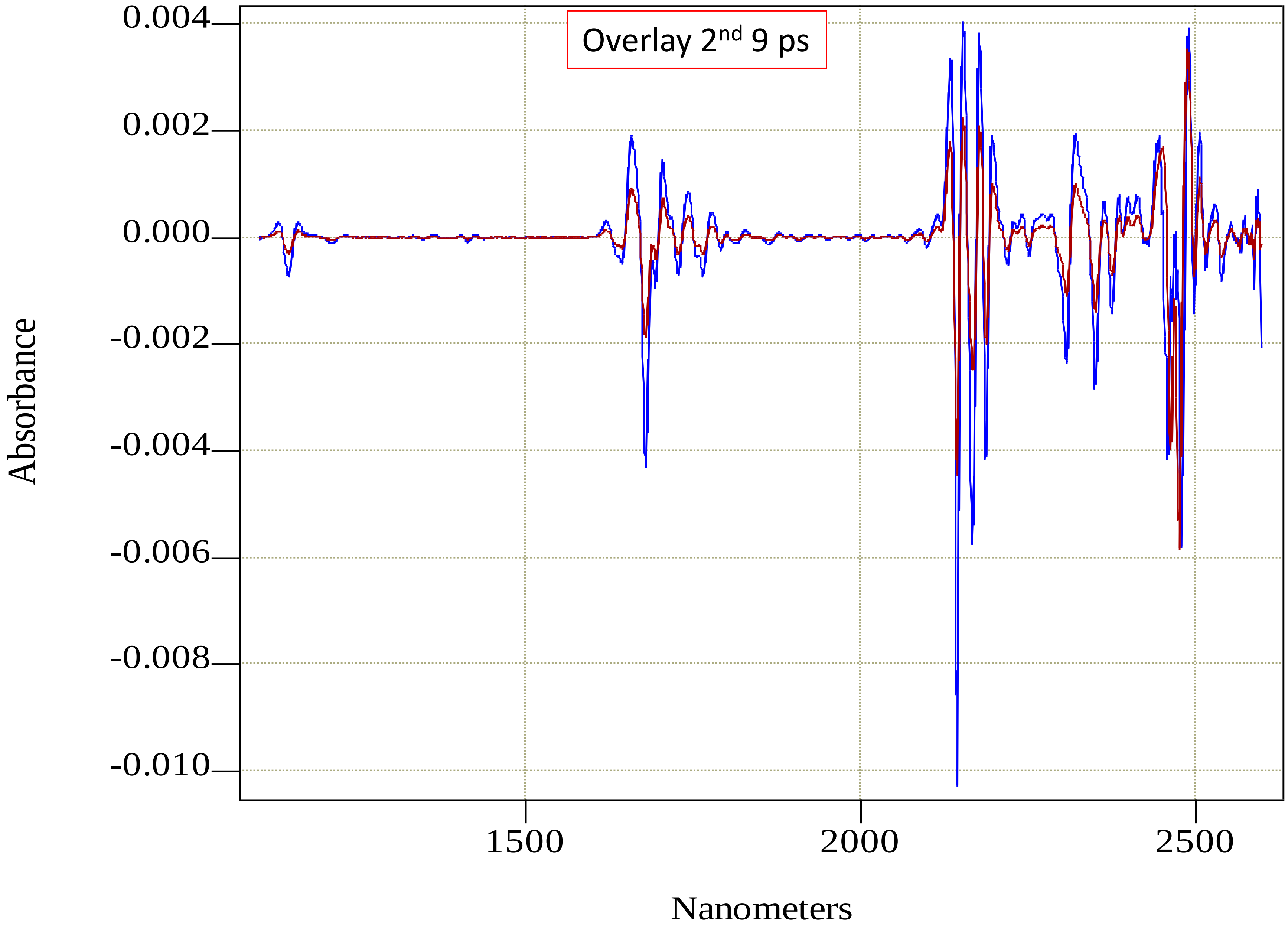
Overlay 1st 5 ps
0.05
0.00
-0.05
Absorbance
1500
2000
2500
Nanometers


Overlay 1st 5 ps
0.04
0.02
0.00
-0.02
-0.04
Absorbance
1600
1650
1700
1750
1800
Nanometers

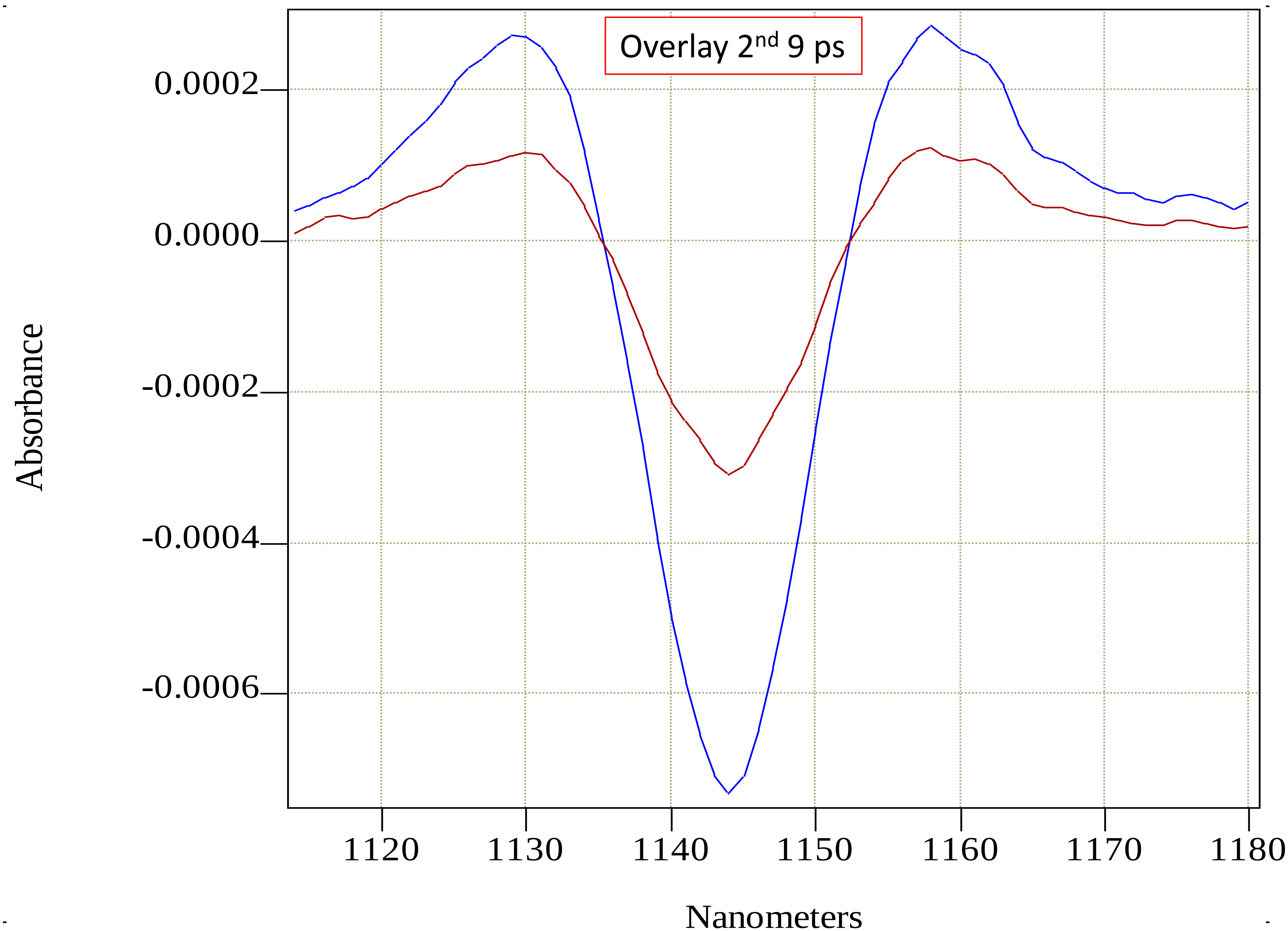


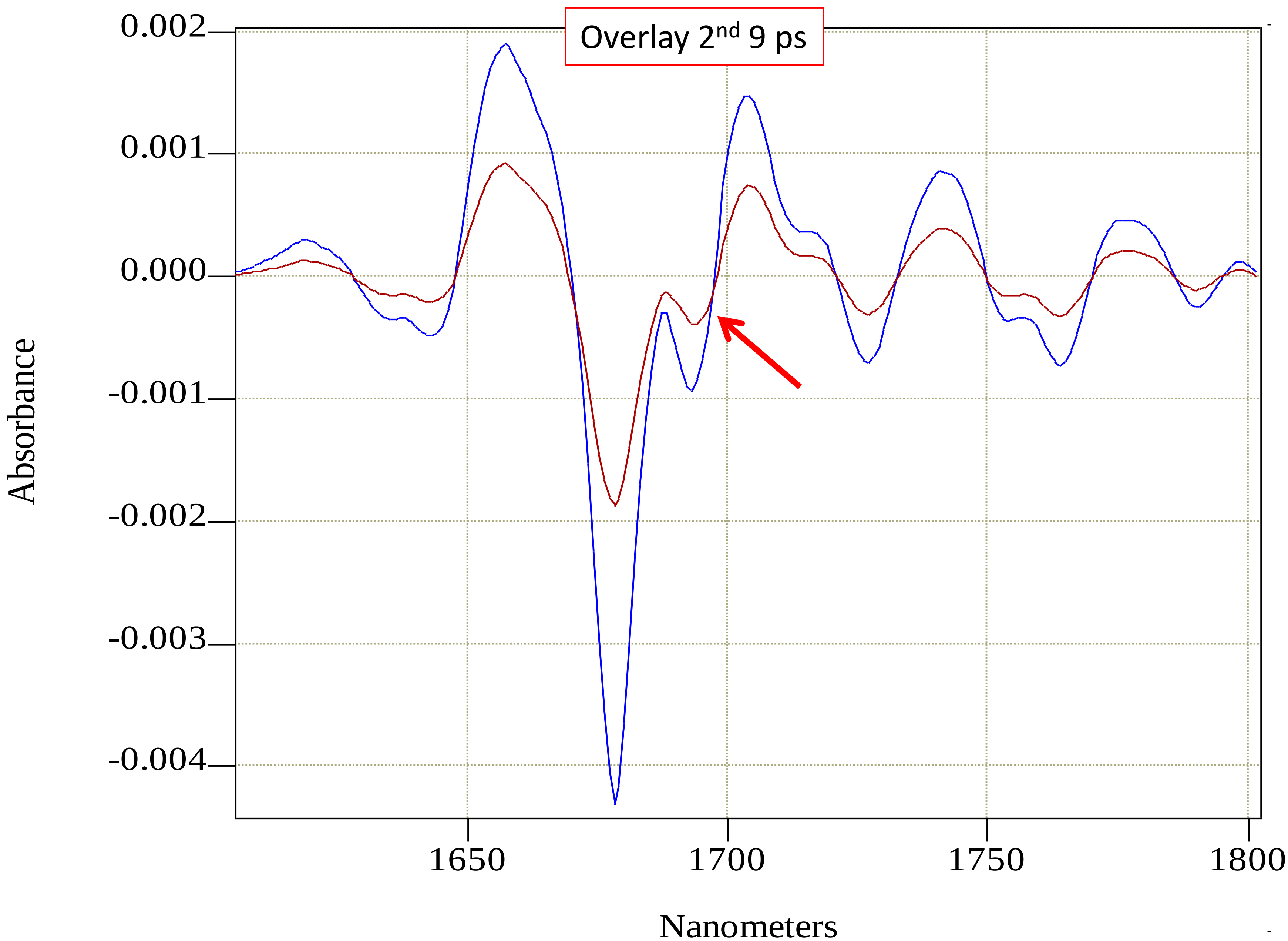
Overlay 1st 5 ps
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
Absorbance
2050
2100
2150
2200
2250
2300
Nanometers

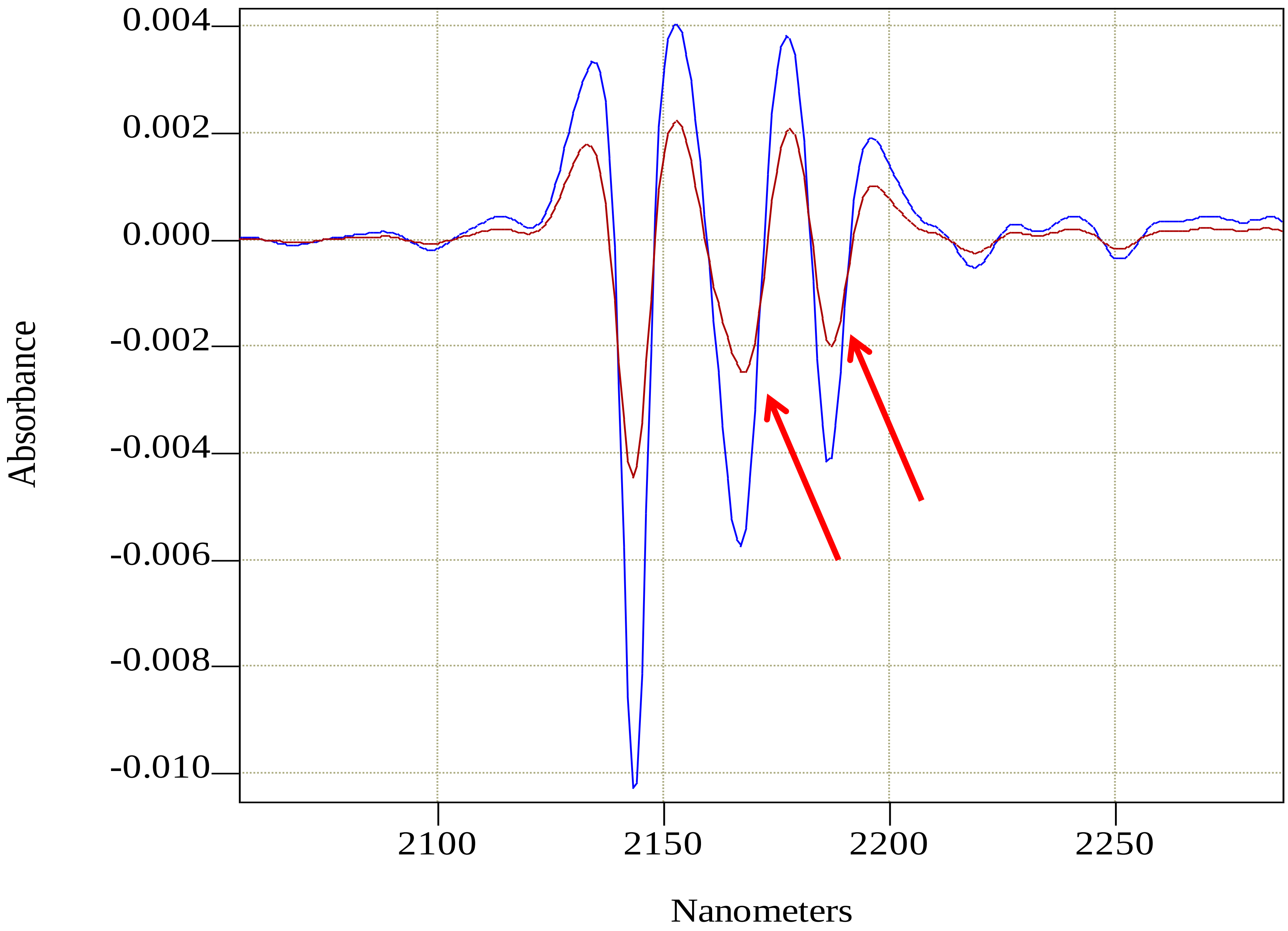
Overlay 1st 5 ps
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
Absorbance
2300
2400
2500
Nanometers

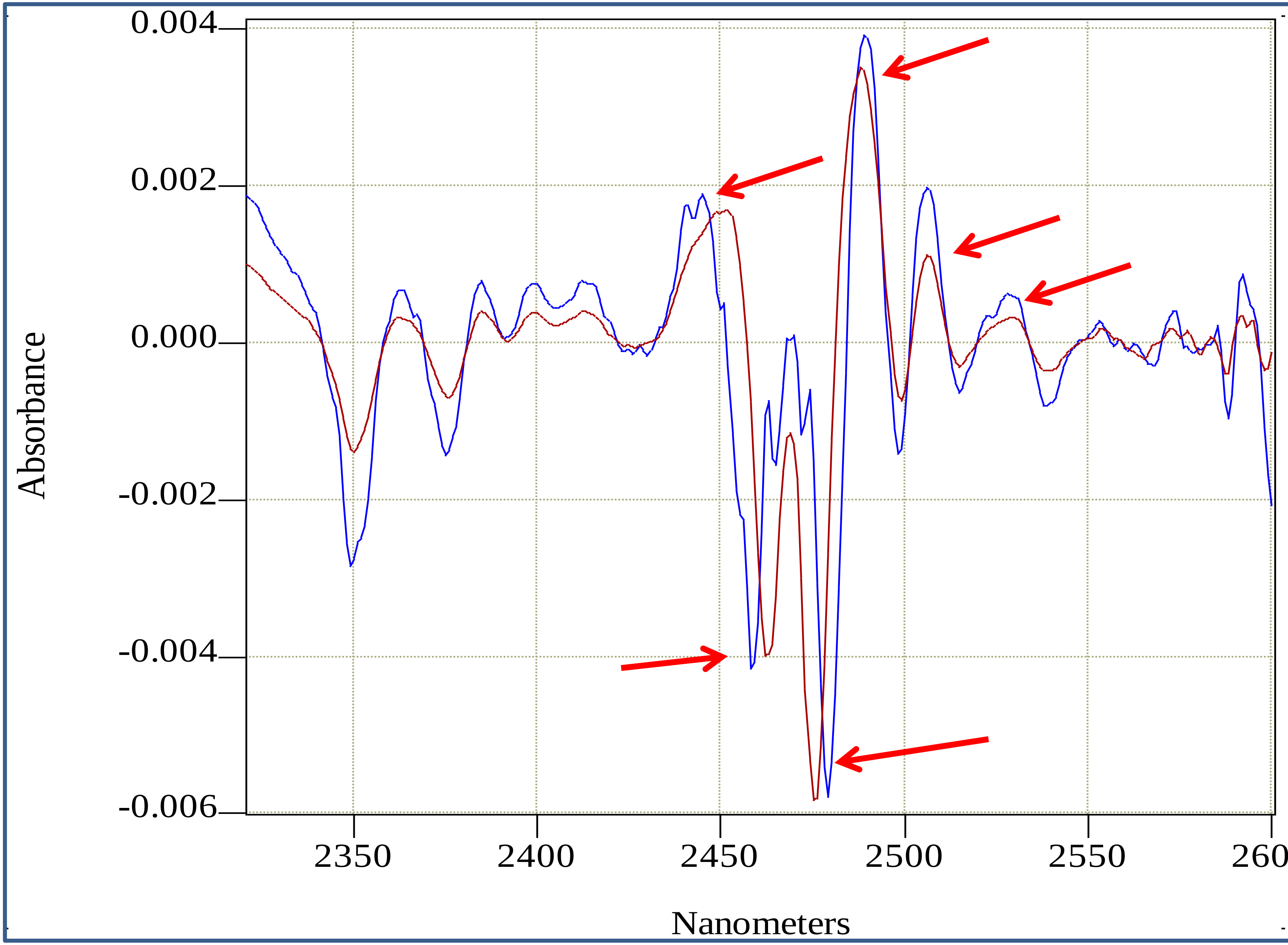


Overlay 2nd 9 ps
0.004
0.002
0.000
-0.002
-0.004
-0.006
-0.008
-0.010
Absorbance
1500
2000
2500
Nanometers


Overlay 2nd 9 ps
0.0002
0.0000
-0.0002
-0.0004
-0.0006
Absorbance
1120
1130
1140
1150
1160
1170
1180
Nanometers


Overlay 2nd 9 ps
0.002
0.001
0.000
-0.001
-0.002
-0.003
-0.004
Absorbance
1650
1700
1750
1800
Nanometers


0.004
0.002
0.000
-0.002
-0.004
-0.006
-0.008
-0.010
Absorbance
2100
2150
2200
2250
Nanometers


0.004
0.002
0.000
-0.002
-0.004
-0.006
Absorbance
2350
2400
2450
2500
2550
2600
Nanometers

Spectrum Differences (wavelength, photometric, and linewidth) vs Prediction, Bias, and Slope Changes

REFERENCES:
(1) Workman Jr, J. and Mark, H., 2017. Chemometrics in Spectroscopy Bias and Slope Correction. *SPECTROSCOPY*, *32*(2), pp.24-30.
Volume 32, Issue 2, pg 24–30

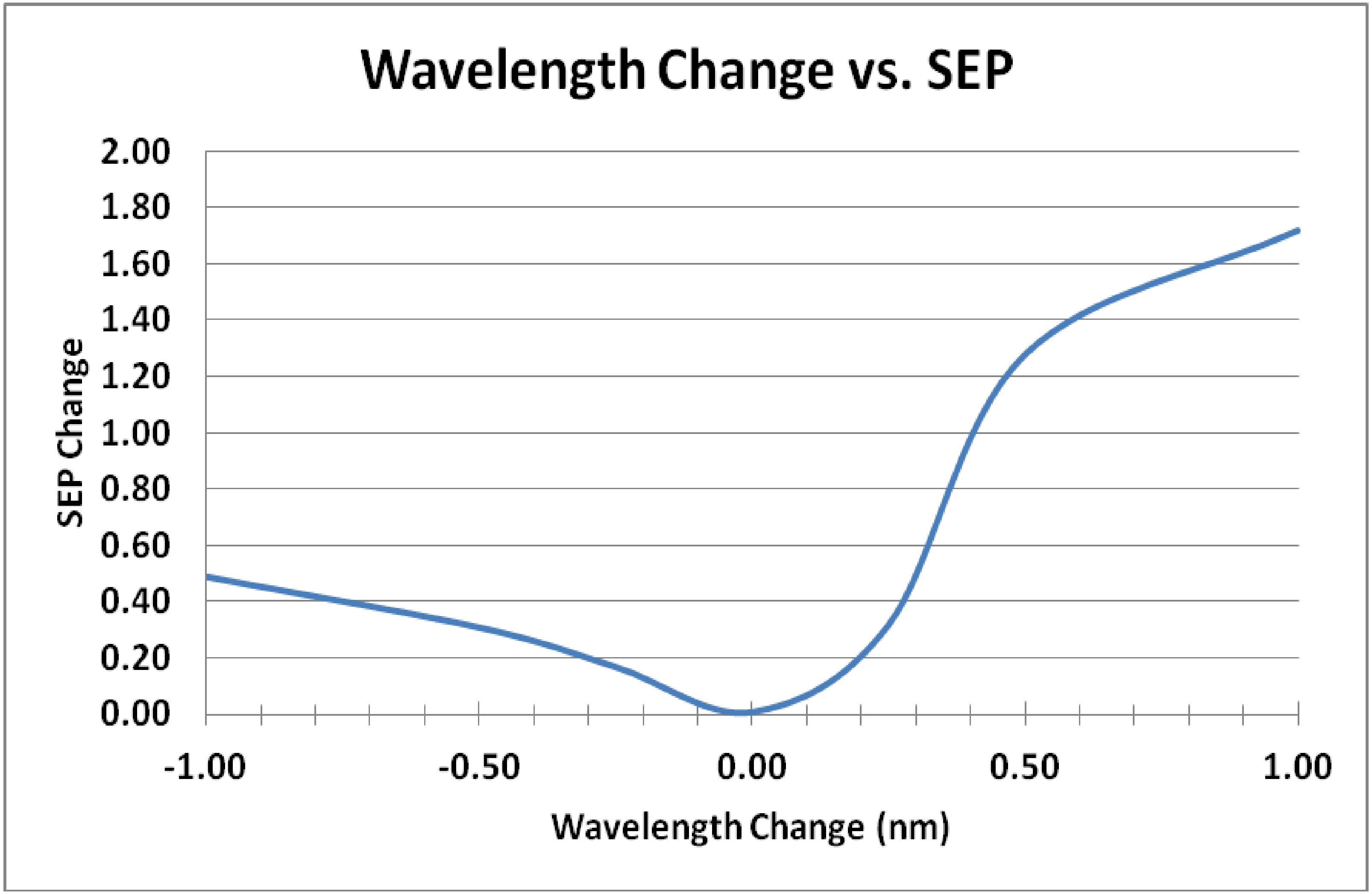
(2) Workman Jr, J. and Mark, H., 2017. Chemometrics in Spectroscopy. Optimizing the Regression Model: The Challenge of Intercept–Bias and Slope “Correction”, *SPECTROSCOPY*, *30*(7), pp. 32–37, 48.

ADDITIONAL REFERENCE:
SA Roussel, B Igne, DB Funk, CR Hurburgh, 2011. Noise robustness comparison for near infrared prediction models. Journal of Near Infrared Spectroscopy 19 (1), 23-36.

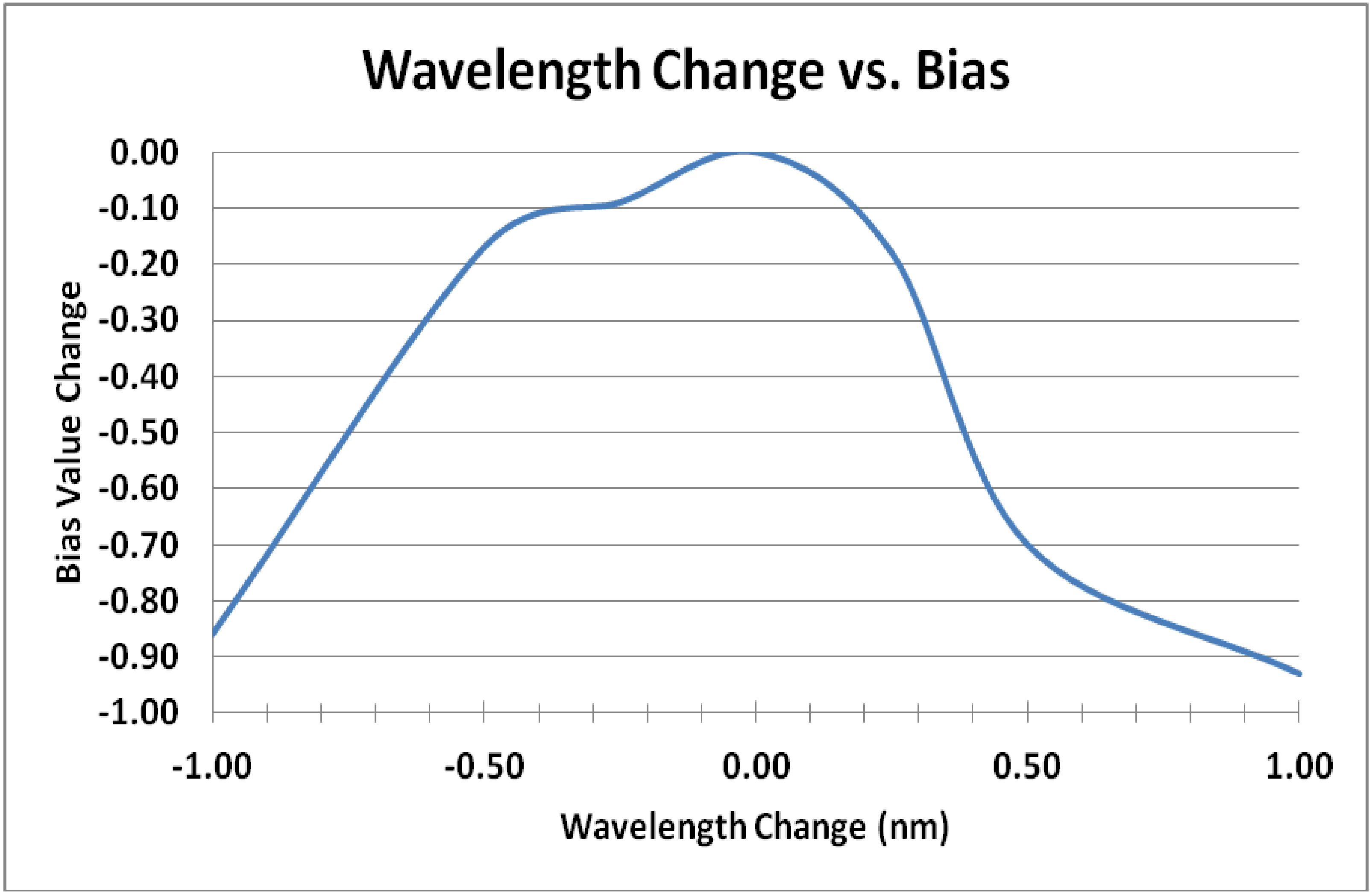
Predicted results for 6 calibration samples with varying wavelength shifts

-1.0 nm	-0.5 nm	-0.25 nm	None	+0.25 nm	+0.5 nm	+1.0 nm
9.65	9.78	9.88	10.00	9.77	9.07	8.76
11.63	11.77	11.87	12.00	11.75	11.03	10.69
13.61	13.76	13.87	14.00	13.74	12.98	12.63
15.59	15.74	15.86	16.00	15.73	14.93	14.57
17.58	17.73	17.85	18.00	17.72	16.89	16.51
19.56	19.72	19.85	20.00	19.71	18.84	18.45

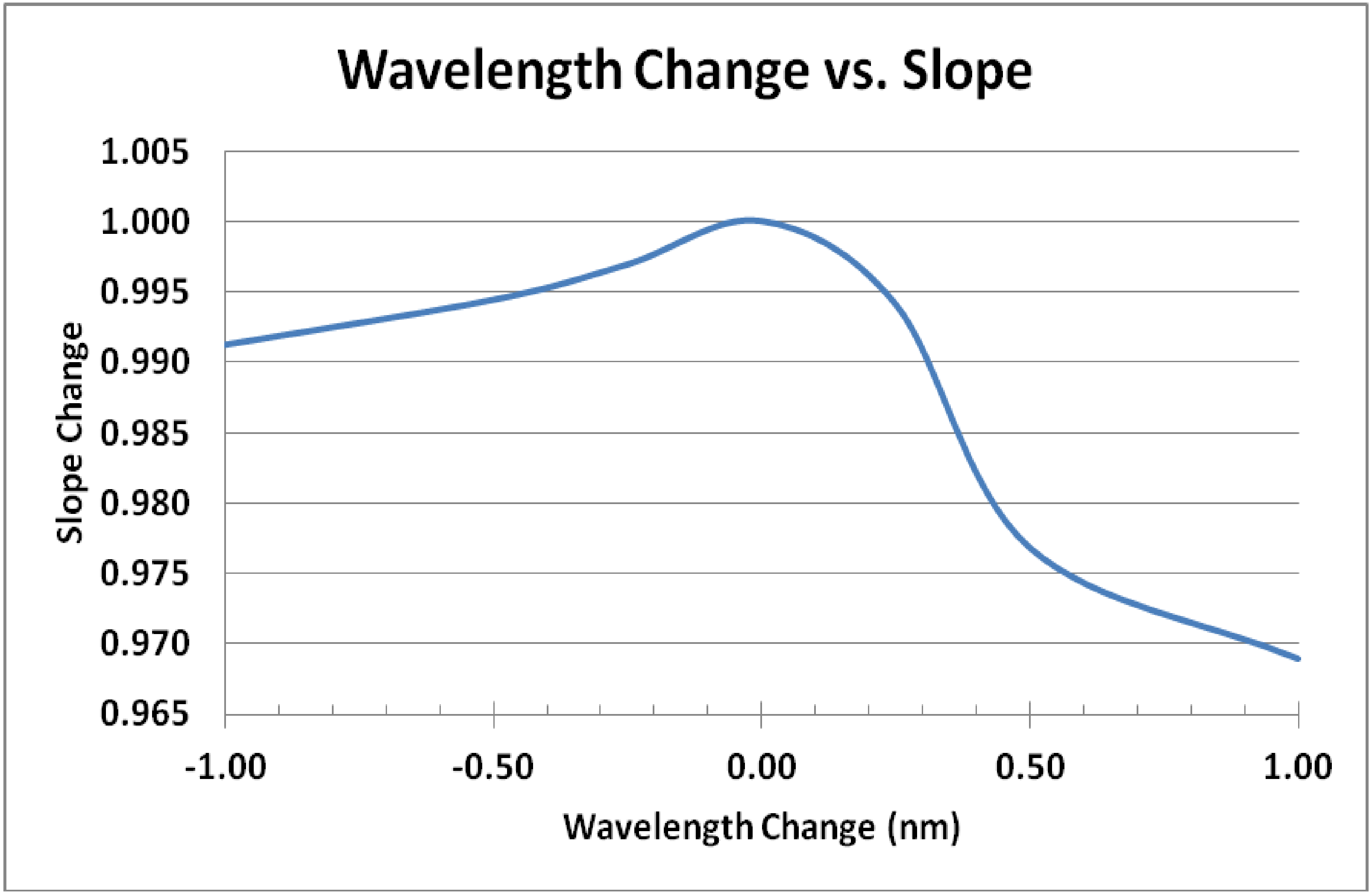
Effect of wavelength shifts



Effect of wavelength shifts



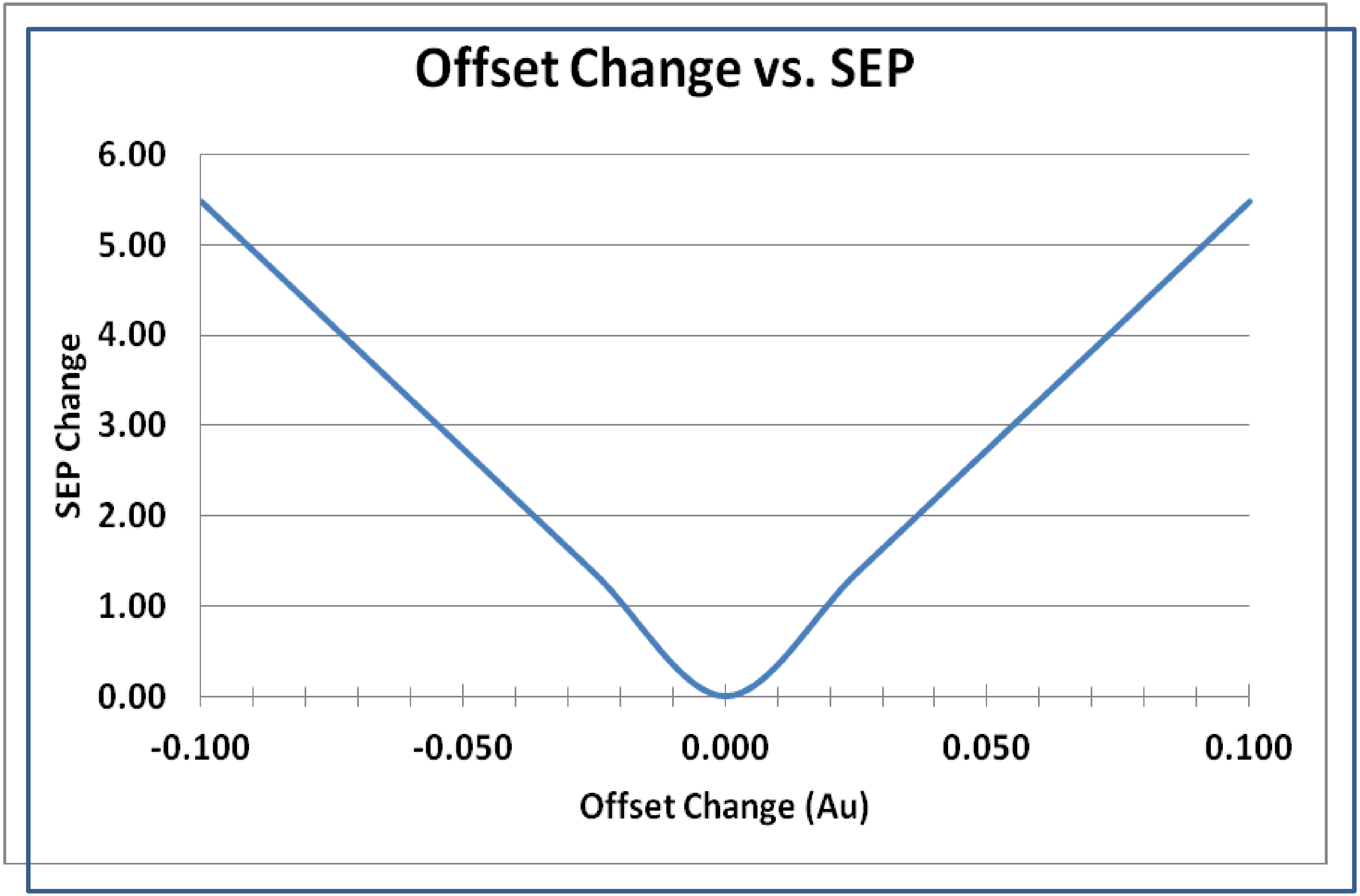
Effect of wavelength shifts



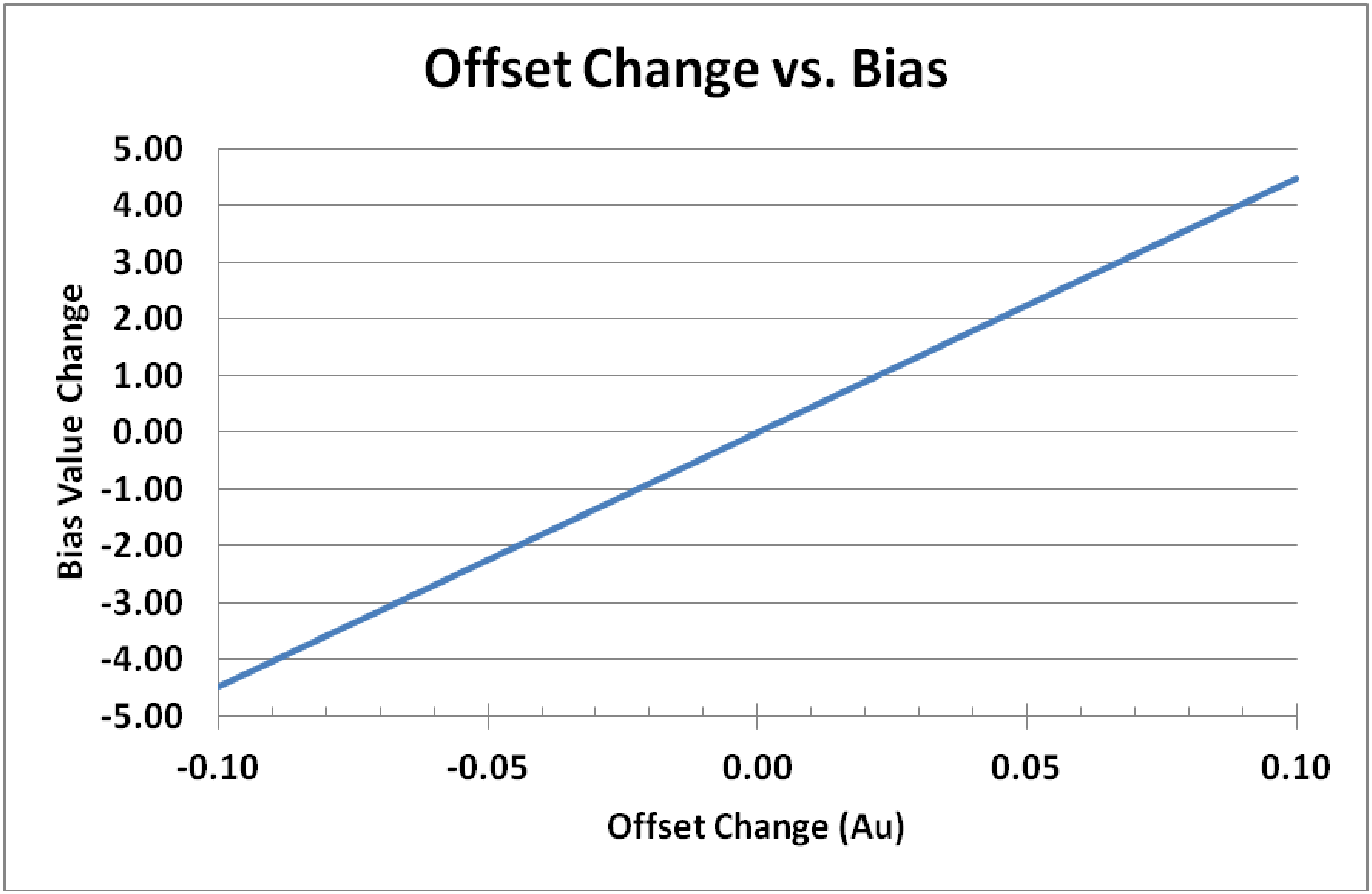
Predicted results for 6 calibration samples with varying photometric offsets

-0.1 A	-0.05 A	-0.025 A	None	+0.025 A	+0.05 A	+0.1 A
5.53	7.76	8.88	10.00	11.12	12.24	14.47
7.53	9.76	10.88	12.00	13.12	14.24	16.47
9.53	11.76	12.88	14.00	15.12	16.24	18.47
11.53	13.76	14.88	16.00	17.12	18.24	20.47
13.53	15.76	16.88	18.00	19.12	20.24	22.47
15.53	17.76	18.88	20.00	21.12	22.24	24.47

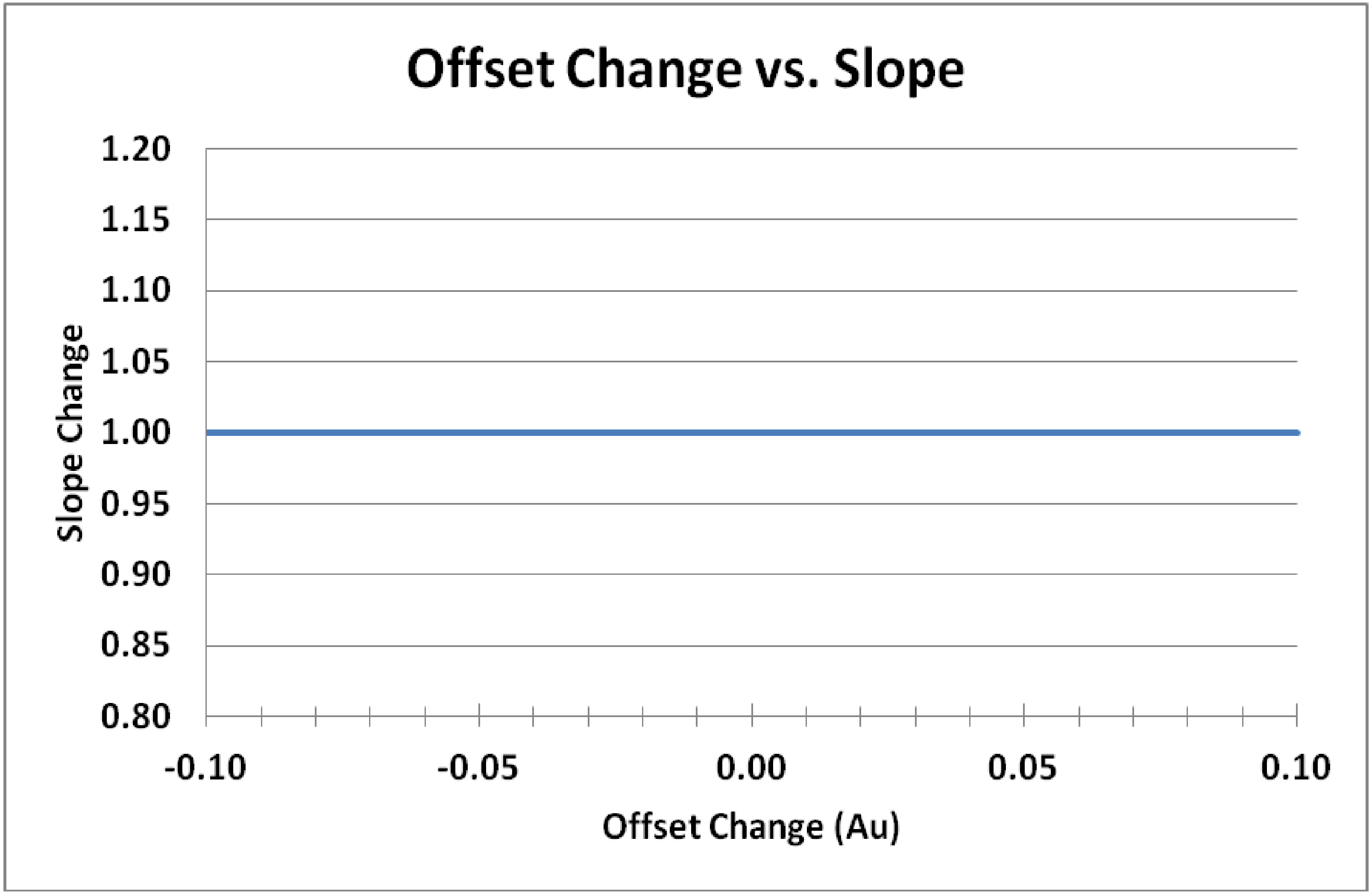
Effect of photometric offset shifts



Effect of photometric offset shifts



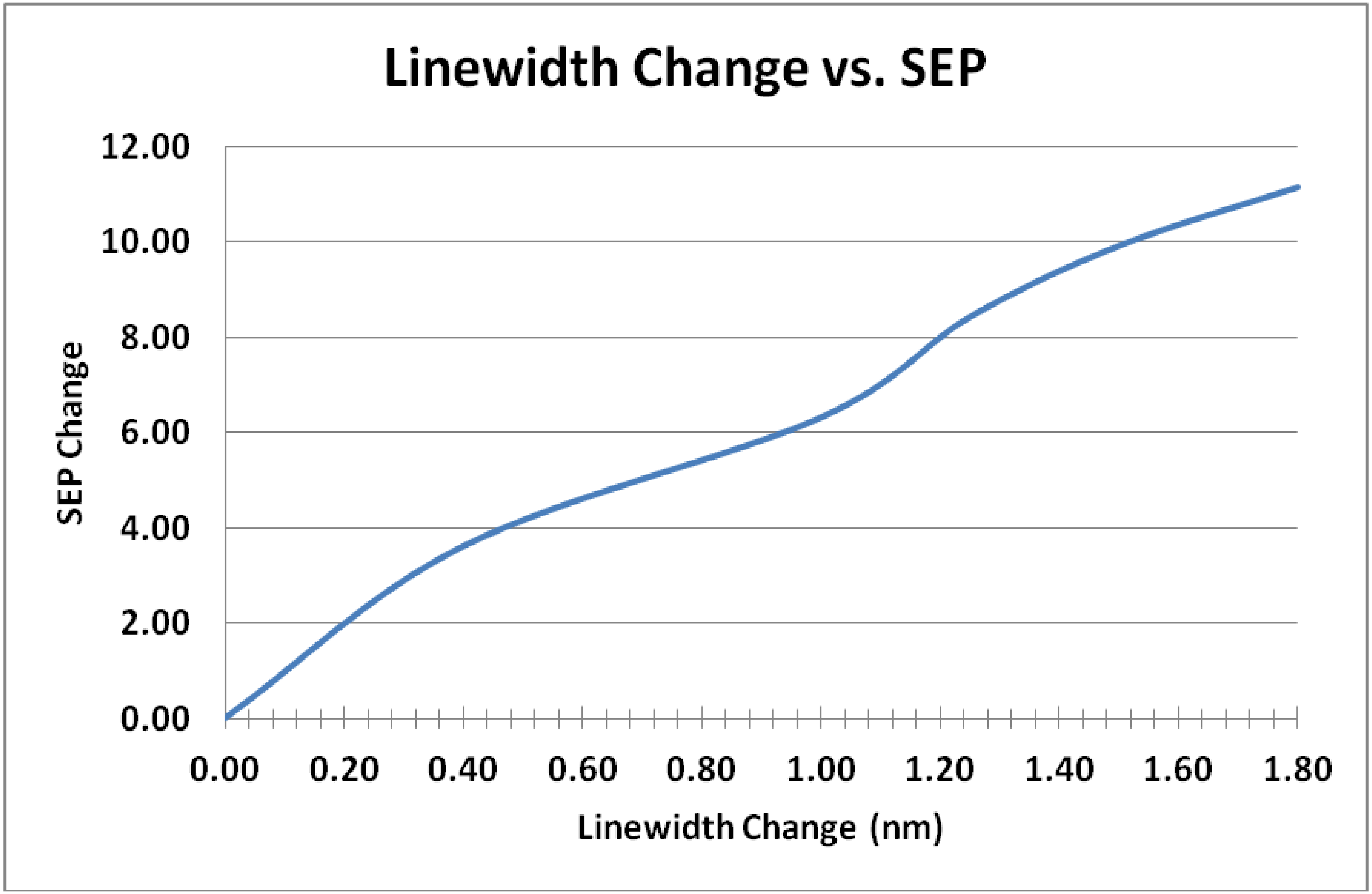
Effect of photometric offset shifts



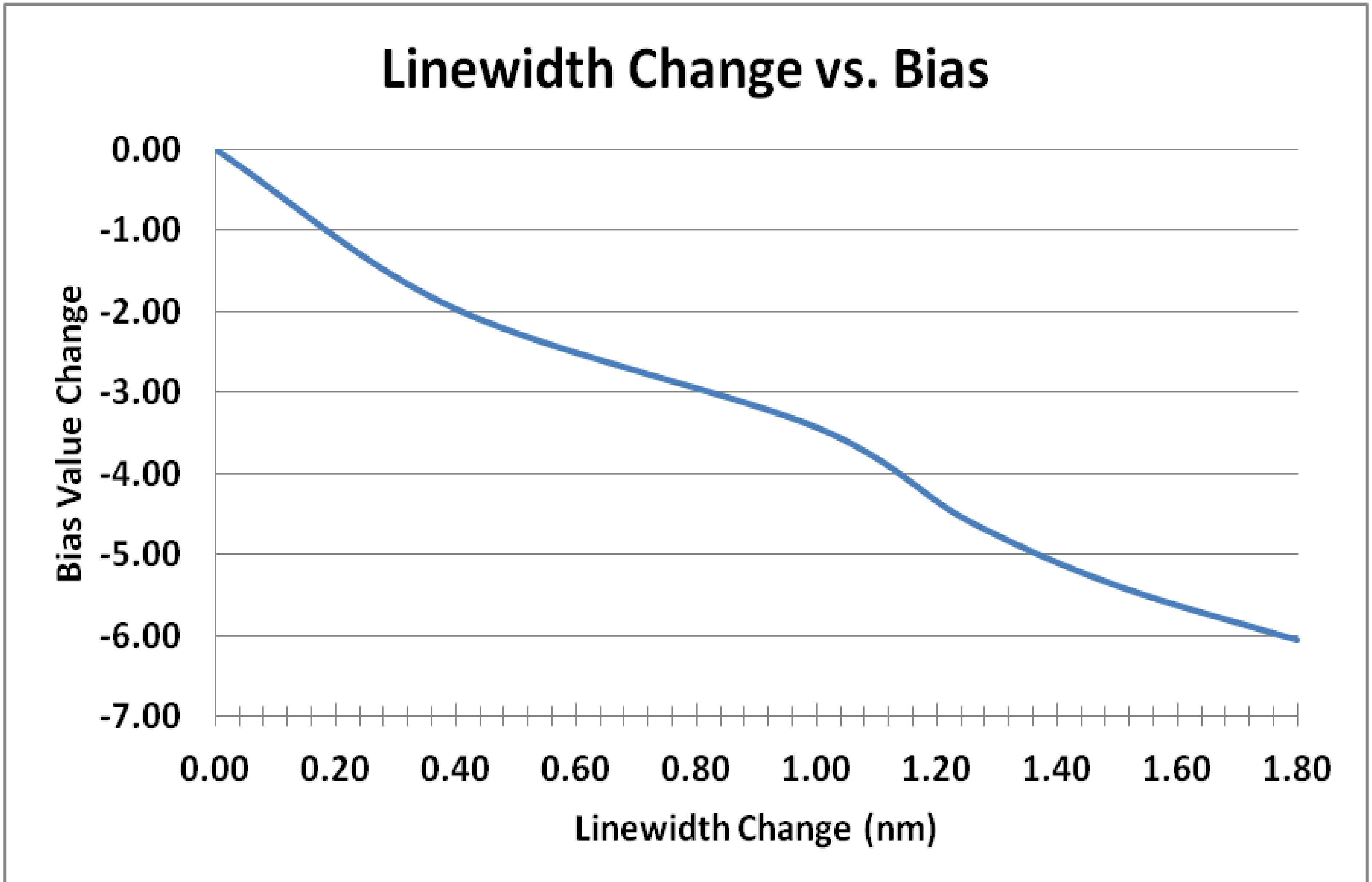
Predicted results for 6 calibration samples with varying linewidths

16.4 nm	16.8 nm	17.4 nm	17.6 nm	17.9 nm	18.2 nm
10.00	7.38	5.43	3.90	2.82	1.93
12.00	9.25	7.20	5.60	4.46	3.53
14.00	11.12	8.97	7.29	6.11	5.13
16.00	12.99	10.74	8.99	7.75	6.72
18.00	14.86	12.51	10.68	9.39	8.32
20.00	16.73	14.28	12.38	11.03	9.92

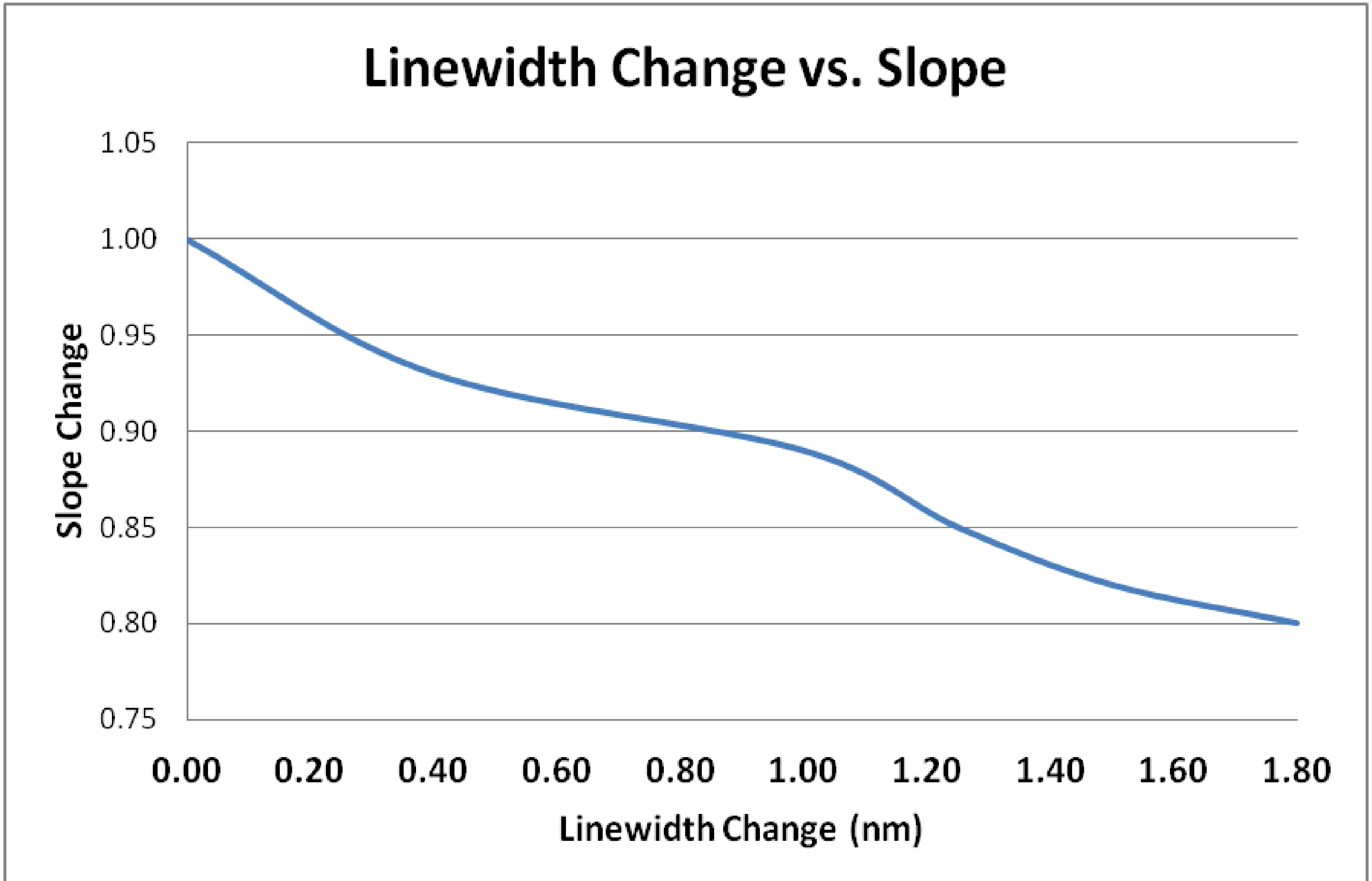
Effect of linewidth changes



Effect of linewidth changes



Effect of linewidth changes



Parameter Change	Amount of Change	Standard Error (SEP)	Conf. Limit (SEP) ±	SIGN. YES/NO	Slope	Slope Sign. ±	Sign. YES/NO	Intercept	Intercept Sign. ±	Sign. YES/NO
Wavelength	-1.00 nm	0.49	0.04	YES	0.9912	0.003	YES	-0.8644	0.011	YES
	-0.50 nm	0.31	0.04	YES	0.9944	0.003	YES	-0.1670	0.011	YES
	-0.25 nm	0.17	0.04	YES	0.9969	0.003	NO	-0.0915	0.011	NO
	0.00 nm	0.01	0.04	NO	1.0000	0.003	NO	0.0000	0.011	NO
	+0.25 nm	0.32	0.04	YES	0.9941	0.003	YES	-0.1763	0.011	YES
	+0.50 nm	1.28	0.04	YES	0.9768	0.003	YES	-0.6954	0.011	YES
	+1.00 nm	1.72	0.04	YES	0.9689	0.003	YES	-0.9325	0.011	YES
Offset	-0.100 A	5.48	0.04	YES	0.0000	0.003	NO	-4.4700	0.011	YES
	-0.050 A	2.74	0.04	YES	0.0000	0.003	NO	-2.2400	0.011	YES
	-0.025 A	1.37	0.04	YES	0.0000	0.003	NO	-1.1200	0.011	YES
	0.000 A	0.01	0.04	NO	0.0000	0.003	NO	0.0000	0.011	NO
	+0.025 A	1.37	0.04	YES	0.0000	0.003	NO	1.1200	0.011	YES
	+0.050 A	2.74	0.04	YES	0.0000	0.003	NO	2.2400	0.011	YES
	+0.100 A	5.48	0.04	YES	0.0000	0.003	NO	4.4700	0.011	YES
Linewidth	0.00 nm	0.01	0.04	NO	0.0000	0.003	NO	0.0000	0.011	NO
	0.40 nm	3.62	0.04	YES	0.9345	0.003	YES	-1.9650	0.011	YES
	1.00 nm	6.32	0.04	YES	0.8856	0.003	YES	-3.4308	0.011	YES
	1.25 nm	8.43	0.04	YES	0.8475	0.003	YES	-4.5746	0.011	YES
	1.50 nm	9.92	0.04	YES	0.8206	0.003	YES	-5.3830	0.011	YES
	1.80 nm	11.15	0.04	YES	0.7983	0.003	YES	-6.0505	0.011	YES

*Confidence limits based upon SEE

N=6 samples

Chemometric methods for Calibration Transfer

Applied Spectroscopy
2018, Vol. 72(3) 340–365

DOI: 10.1177/0003702817736064
journals.sagepub.com/home/asp
SAGE

A Review of Calibration Transfer Practices and Instrument Differences in Spectroscopy

Jerome J. Workman Jr[1,2]

Abstract

Calibration transfer for use with spectroscopic instruments, particularly for near-infrared, infrared, and Raman analysis, has been the subject of multiple articles, research papers, book chapters, and technical reviews. There has been a myriad of approaches published and claims made for resolving the problems associated with transferring calibrations; however, the capability of attaining identical results over time from two or more instruments using an identical calibration still eludes technologists. Calibration transfer, in a precise definition, refers to a series of analytical approaches or chemometric techniques used to attempt to apply a single spectral database, and the calibration model developed using that database, for two or more instruments, with statistically retained accuracy and precision. Ideally, one would develop a single calibration for any particular application, and move it indiscriminately across instruments and achieve identical analysis or prediction results. There are many technical aspects involved in such precision calibration transfer, related to the measuring instrument reproducibility and repeatability, the reference chemical values used for the calibration, the multivariate mathematics used for calibration, and sample presentation repeatability and reproducibility. Ideally, a multivariate model developed on a single instrument would provide a statistically identical analysis when used on other instruments following transfer. This paper reviews common calibration transfer techniques, mostly related to instrument differences, and the mathematics of the uncertainty between instruments when making spectroscopic measurements of identical samples. It does not specifically address calibration maintenance or reference laboratory differences.

Comparison of Transfer Methods (1)

- **Instrument Alignment and Correction.**
- **Filter Instrument Calibration Transfer.**
- **The Master Instrument Concept.**
- **Piecewise Direct Standardization (PDS).**
- **Orthogonal Signal Correction (OSC).**
- **Procrustes Analysis (PA).**
- **Finite Impulse Response (FIR).**
- **Maximum Likelihood Principal Component Analysis (MLPCA).**
- **Successive Projections Algorithm (VSPA).**
- **Compressed Wavelet Domain Standardization (WTDS).**
- **Canonical Correlation Analysis (CCA).**

Comparison of Transfer Methods (2)

- **Positive Matrix Factorization (PMF).**
- **Spectral Regression (SR).**
- **Wavelet Packet Transform Standardization (WPTS).**
- **Stacked Partial Least-Squares (SPLS) Regression.**
- **Multiplicative Signal Correction (MSC).**
- **Classification Methods.**
- **Synthetic Calibration Spectra.**
- **Dispersive to FT Transfer.**
- **Dispersive to Handheld Transfer.**
- **Temperature Compensation.**
- **Two-Dimensional Method Transfer.**

Comparison of Transfer Methods (3)

- **Developing Global or Robust Models Including Variation Between Instruments.**
- **Augmenting Models Over Time.**
- **Sample Selection to Improve Spectral Data.**
- **Spectral Data Transformation.**
- **Special Standardization Mathematical Approaches.**
- **Locally Weighted Regression (LWR) Methods.**
- **Use of Indicator Variables.**

Mathematical Tests for Calibration Transfer (1)

- **Comparisons When Transferring Calibrations.**
- **Bias or Slope Adjustments of Predicted Results Across Parent and Child Instruments.**
- **Bias (Means) One-Sample t-Test Between Parent and Child Instruments.** The concept of
- **Bias (Means) Two-Sample t-Test Between Parent and Child Instruments.** If the predicted
- **Comparing the Correlation Coefficients Between Parent and Child Instruments Using the (r-to-z Transform) Significance Test.**
- **Slope Significance Limit Test Between Parent and Child Instruments.**

How to Tell if Two Instrument Predictions are Statistically Alike (1)

- **Relative Standard Uncertainty**
- **Bland-Altman Test as a Measure of Limits of Agreement.**

Q&A