

Unity Scientific White Paper

Near-Infrared Spectrometers:  
A Guide to Evaluating Instrument  
Calibration and Performance

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This whitepaper was compiled as a guide to evaluating NIR instrument performance and the diagnostic tests use to evaluate performance. Please direct any questions to Dr. Jerome Workman Jr., PhD. at [jworkman@unityscientific.com](mailto:jworkman@unityscientific.com).

# 1 Overview

The essential basics of true instrument calibration, validation and maintenance are discussed in detail. A series of tests for measuring wavelength accuracy and repeatability, photometric accuracy and repeatability as well as noise and the related signal to noise ratio factor is described. All parameters which are important for achieving accuracy, repeatability and transferability of calibrations used with Near Infrared instrumentation are discussed and evaluated. A set of NIST traceable standards have been measured on a wide range of commercially available instruments and comparative results are presented for Unity Scientific SpectraStar™ XL, Bruker Tango, Büchi NIRFlex N-500 & FOSS NIRStm DS2500.

## 1.1 The Basics of NIR Measurements

Near-infrared (NIR) spectrometers are a special type of instrument requiring the disciplines of engineering, physics, analytical chemistry, chemometrics, and computer science. The unique aspect of NIR spectrometers over other spectrophotometric methods is the requirement for the instrument to be calibrated using multivariate calibration methods and to remain calibrated over extended periods of time. Most other spectrometers are used for qualitative analysis or are calibrated at least once every day just prior to use for analysis. Due to the significant number of samples and reference analysis required, NIR spectrometers are calibrated only as often as required. This may mean that an instrument is expected to produce accurate results over days, weeks, and months, using only a few samples to monitor performance over time. Such a stringent requirement is unique to all spectrophotometric methods. Thus the additional disciplines of metrical sciences are required to ensure consistent collection of raw data for the optimum application of NIR. Metrical sciences include the concepts of repeatability, reproducibility, accuracy, and such concepts as standard uncertainty and relative standard uncertainty. Metrical sciences involve the use of first principles science and the use of measurement materials that are well characterized and stable over time referencing all measurements to primary physical standards and National Laboratory traceable standards. These reference materials are used to calibrate instrumentation to a "first principles" steady state or stable position so that measurements are traceable, accurate and repeatable over time. First principles is the measurement practice used around the world by national laboratories for

all commerce and standards for liquids, solids, and gas measurements. Using a “master” instrument concept or unstable material as a reference is quite risky over time, since the reference instrument will change over time, and if the reference is changing then there can be no certainty in the reproducibility/accuracy of measurement results. Additionally, the reference measurements become instrument dependent and this will hinder data transfer to other instrument types or use of data for future generation instruments. If the instrument basis of calibration is constructed using stable and well-characterized physical phenomena then the instrument condition or status is always known as compared to its initial condition or state, and calibrations developed on the instrument will always predict accurately on a properly calibrated system.

This is a point where one could discuss two types of calibration for NIR instruments. The first calibration is used to align the spectrometer performance for precise and accurate response for wavelength registration, photometric (absorbance) registration, line shape and resolution, linearity in detector response, and stray light characteristics. The second type of calibration is measuring product samples and building multivariate calibrations for prediction of parameters such as protein, fat, moisture, and the like.

Once the initial performance calibration is performed by aligning aspects of the instrument with a special set of reference materials, the instrument is ready to collect the product sample data (spectra) to create a multivariate calibration for the application of interest. Now whenever the instrument is tested it can be aligned to the original set of stable reference materials; this gives the product spectral data the integrity required for efficient application of NIR technology. At any time if a lamp fails or major components are replaced on the instrument it can immediately be brought back to a precise steady-state condition using the special reference materials and a set of special alignment algorithms. So the instrument is always maintained to give the same or identical spectral results for every product measured. When each instrument is aligned at manufacturing with the special set of reference standards, they are literally all identical or alike. Furthermore at any time they can be realigned to the standards and made to measure identically to the day they were manufactured. When instrumentation is aligned properly using first principle references, they can be treated as a population of alike instruments.

## **1.2 The Basics of Calibration Modeling**

Various methods have been proposed to produce the universal model or a calibration that is mostly robust against the typical instrument variations that are common to modern commercial instruments. These have been referred to as robust models, or global models. In this case various experimental designs are constructed to better represent the product, reference values, and instrument variations within the model so that predicted values will be more accurate over time and sample changes. Using this approach one might design a factorial experiment for the composition of the learning or calibration set to include multiple variations typically encountered during routine analysis. A list of some of these variations may consist of: differences in pathlength, sample temperature, moisture content, flow rate, particle size, interferent content, instrument design type, constituent ratios, sampling parameters, and the like [1]. These approaches will work for a period until the instrument drifts or the product or constituent chemistry changes. These types of changes are expected and thus routine recalibration (i.e., model updating) would normally be required as a standard procedure if any of the product or reference laboratory method changes are considered significant. These changes are not related to the NIR spectrometer performance and are not addressed in this discussion.

## **1.3 Instrument Types**

Spectrometers, or more appropriately, spectrophotometers, come in many design types. There are instruments based on the grating monochromator with mechanical drive, grating monochromator with encoder drive, the Michelson interferometer in various forms, dispersive gratings with array detectors, interference and linear variable filter instruments with single detectors, linear variable filters with array detection, MEMS based Fabry-Perot interferometers, Digital Transform actuator technology spectrometers, Acousto-optic tunable filters (AOTF), Hadamard transform spectrometers, laser diodes, tunable lasers, various interference filter types, multivariate optical computing filters, and others. Each of these technologies, although, they operate in the same spectral domain, has their own strong and weak points. As long as they are not strictly calibrated versus officially accepted standards they might exhibit significant differences in the shape and character of the spectra they generate.

## **2 Instrument Comparison and Evaluation Methods**

There are many standard tests that are used to determine quality and likeness between spectrophotometer instruments and several of those tests will be described in this paper. Eight basic tests and a summary evaluation are described here as a rigorous set of standard methods to determine instrument measurement performance, including: wavelength accuracy, wavelength repeatability, absorbance/response accuracy, absorbance/response repeatability, photometric linearity, photometric noise, signal averaging (noise) tests, and the instrument line shape (ILS) test. If carefully conducted, these experiments provide specific information for diagnosing mechanical, optical, and electronic variations associated with design or manufacturing limitations. They provide objective data for correcting and refining instrumentation quality and likeness. These methods combined with stable and traceable standards are useful for providing precise instrument alignment and calibration continuously over the lifetime of an instrument [References 1-8].

### **2.1 Instrument Optical Quality Performance Tests**

The following series of tests are used to qualify instrument performance and to determine which issues are problematic due to deficiencies in instrument design features or loose manufacturing tolerances. These tests are related to likeness in measurement performance between instruments and to overall accuracy and precision (as repeatability and reproducibility) and are based on certified reference standards. Note that the terms optical density (O.D.) and absorbance units (AU) are synonyms. (Note that "Optical density" is found in historical documents, and is still used in physics, and biomedical and optical engineering, but not as often used in analytical chemistry.) A brief explanation of each test is found below with a more extensive explanation and statistical definition is listed in the Appendix.

### **2.2 Wavelength Accuracy**

Wavelength accuracy is determined by analyzing a standard reference material with stable, narrow and well defined peaks and comparing the calculated peak positions on the instrument to the known or reference positions. Wavelength accuracy is described as deviations from the known peak positions with lower values being best. Wavelength accuracy defines the accuracy

of the X axis and high wavelength accuracy is critical for stable calibrations and calibration transfer.

### **2.3 Wavelength Repeatability (Precision)**

Wavelength repeatability is related to wavelength accuracy in that the same standard reference material with well-defined peaks is normally used for this test. Wavelength repeatability is determined by analyzing the reference material a set number of times and calculating the standard deviation of each peak position, with lower values being best. Wavelength repeatability describes the reliability of the X axis positions and is important to both calibration performance and calibration transfer.

### **2.4 Absorbance or Photometric Accuracy**

Absorbance accuracy describes how close the spectrophotometer measures and reports the absorbance of a known reference standard. Typically a reflectance standard of close to 100% reflectance is measured on the instrument and the absorbance calculated and compared to the reference value. Absorbance accuracy is important for calibration transfers and stability.

### **2.5 Absorbance or Photometric Repeatability**

Absorbance repeatability uses the same standards as the accuracy test above but uses replicate measurements to determine the standard deviation of the replicates. Absorbance repeatability is an indication of the stability and performance of the spectrophotometer.

### **2.6 Photometric Linearity**

Photometric linearity is determined by scanning a number of reference standards of varying reflectance in the instrument and comparing the expected response to the response observed. A regression line is plotted for both the expected and observed responses and the linearity and slope of each is compared. Photometric linearity describes the response of the spectrophotometer across samples of low and high photometric absorbance and is important to the performance of the calibration models.

## **2.7 Photometric Noise**

Photometric noise is the base level of background signal in the spectrophotometer that is present in all measurements. The noise is a function of all the instrument components including electrical noise, environmental changes, mechanical noise, component positioning errors, etc. Photometric noise is measured by taking replicate measurements of a reflectance standard and looking at the standard deviation of the difference. Ideally the replicates should be identical and the noise equal to 0.

## **2.8 Stray Light**

Stray light is the amount of light that reaches the detector that is not part of the measurement. This light originates from the lamp reflecting internally within the spectrometer and striking the detector, and it also originates from non-measurement light going through the optics to the detector. The lower the stray light the more accurate the peak heights and shapes will be, especially for higher absorbing samples. It is measured using the difference between the actual measurements from the instrument and the known reference values for reflectance standards.

## **2.9 Dark noise**

Dark noise is the amount of noise the instrument generates from its electronics and mechanical operation. It indicates the quality of the instrument electronics and the quietness of operation for the instrument. Each spectral measurement is ratioed to the dark current and so the lower the dark noise, the quieter the performance of the instrument. Low dark noise will yield more precise and accurate analytical values.

## **2.10 Bandpass or line shape**

The bandpass or line shape is important in transferring calibrations and in maintaining sufficient resolution in the spectrometer to provide reliable spectral data. The fine structure of product sample spectra is maintained when the line shape is constant. The spectrometers must maintain constant line shape over the spectral range for transfer of calibrations. The integrity and structure of the measured spectra depend on an instrument with reliable, sufficient, and repeatable line shape.



### 3 Measuring Instrument 'Alikeness'

There are some basic performance criteria that indicate a reasonable likeness between two or more instruments. Specific calibrations and prediction performance criteria will vary and so will the comparative instrument performance metrics as shown in Table 1.

Table 1. Comparative performance metrics for spectrometers

Wavelength accuracy	Absolute deviation should be less than $\pm 0.5$ nm versus NIST reference following calibration using NIST traceable reference materials (measurements for a specified set of stable reference peaks)
Wavelength repeatability	$< 0.05$ nm (1 sigma)
Absorbance accuracy	Absolute deviation must be less than $\pm 0.05$ Au versus NIST traceable reference standard
Absorbance precision	$< 0.001$ AU (1 sigma)
Photometric linearity	Slope: $1.00 \pm 0.02$ ; Intercept: $\pm 0.02$ (Absolute) for method
Photometric noise	RMS $< 0.000020$ AU for 0.0

#### 3.1 Results from evaluation of the different NIR instruments

The use of excellent design, quality components, and good manufacturing practices enable different instrument designs to perform well. However if there is not a reliable use of reference materials to measure the instrument performance against and to adjust the instrument on a regular basis any instrument will drift and not perform well when using multivariate calibrations. Therefore the pure concept of first principles alignment to officially accepted reference standards is the most reliable and future-proof approach available to correct the instrument performance at any time. To demonstrate this we looked at the performance of several commercial instruments and compared the results in the following table. The noise is described over the wavelength regions specified as well as the S/N or signal to noise, which is computed as the ratio of the reflectance value to the RMS noise of the instrument for repeated measurements. Table 2 demonstrates a comparison in performance metrics for four commercial spectrometers under identical measurement conditions. Each spectrometer was checked and had passed the individual vendor diagnostics.

Table 2. Performance comparison of multiple commercial instruments (identical tests and samples)

Parameter	SpectraStar 2500XL-R	Foss NIRSTM DS2500	Bruker Tango	Büchi NIRFlex N-500
$\lambda_{nm}$ Accuracy <sup>1a</sup>	-0.40	-1.43	-0.31	-1.23
$\lambda_{nm}$ Accuracy <sup>1b</sup>	-0.79	-5.14	-3.38	-2.25
$\lambda_{nm}$ Accuracy <sup>2</sup>	-0.23	0.36	-0.79	-0.71
$\lambda_{nm}$ Precision <sup>1c</sup>	0.014	0.023	0.000	0.048
Photo Accuracy <sup>3</sup>	0.04	-0.005	-0.220	-0.126
Photo Precision <sup>3</sup>	35e-5	13.7e-5	125e-5	75.7e-5
Linearity ( $R^2$ ) <sup>1d</sup>	0.993	0.976	0.991	0.966
Ave. Stray Light <sup>1d</sup>	1.3%	1.0%	0.20%	4.5%
Noise 680-2500 <sup>3</sup>	66e-6	61e-6	NA	NA
Noise 1100-2500 <sup>3</sup>	19e-6	42e-6	518e-6	168e-6
Noise 1500-2500 <sup>3</sup>	13e-6	45e-6	583e-6	135e-6
Noise 2350-2500 <sup>3</sup>	24e-6	57e-6	816e-6	79e-6
S/N 680-2500 <sup>3</sup>	15133	15933	NA	NA
S/N 1100-2500 <sup>3</sup>	52925	22689	1446	5952
S/N 1500-2500 <sup>3</sup>	74254	21618	1285	7407
S/N 2350-2500 <sup>3</sup>	41286	16937	918	12658

<sup>1a</sup> (3 Wavelength Standard - R99Polystyrene, 10 nm bandwidth), <sup>1b</sup> (8 Wavelength Standard - R99Polystyrene, 10 nm bandwidth), <sup>1c</sup> (2 Wavelength Standard - R99Polystyrene, 10 nm bandwidth), <sup>2</sup> (11 Wavelength Standard - SRM 1920a, 10 nm bandwidth), <sup>1d</sup> (Effective stray light for 5 peak heights using Standard - R99Polystyrene), <sup>3</sup> (Reflectance/photometric standard - R99, RMS and S/N are for 3 static replicates),

## 4 Discussion

The data presented above demonstrate that the optical performance and reference basis differs among the various instrument types. Some of the performance differences are based upon the performance limitations of the technology employed. For example, scanning monochromators such as the SpectraStar XL and DS2500 show very good noise characteristics, while FT instruments are typically demonstrate very good wavelength repeatability. Other performance values such as photometric and wavelength accuracy tests reflect the use of various references, from first principle based certified reference standards to those based on a chosen master instrument to no reference at all in some cases. Instruments that have poor optical performance and alignment will demonstrate poor calibration performance and accuracy over time. They will require continuous calibration adjustment and the measurement of product samples.

Additionally, the data above illustrate the root cause of data transfer issues across instruments using differing or unstable references. As long as all calibration data is collected on instruments calibrated using the same reference that are similar enough, calibrations can be re-used within that group. If similarity is not sufficient or the references not fixed, it is usually recommended to add spectra from the different instruments into the same calibration model to stabilize the model for instrument to instrument variations. This process adds the noise and spectral variation from the parent and child instruments and forces the model to compensate for the variation from both spectrometers. The practice of blending spectral data with different wavelength and photometric characteristics degrades the signal to noise for the final calibration. Future white papers will discuss the effects poor instrument calibration has on the accuracy and repeatability of constituent predictions

In summary, the variations in the values above demonstrate the importance of having a consistent basis of instrument calibrations. Having absolute control of the optical properties of the analyzer for the measurement properties of: wavelength accuracy, wavelength repeatability, absorbance/response accuracy, absorbance/response repeatability, photometric linearity, photometric noise, signal averaging (noise) tests, and the instrument line shape (ILS) one can ensure that data generated are safe for the future and will give the same results on any current or future instruments that are properly manufactured and calibrated.

## 5 Conclusion

We have shown the ways to measure instrument performance and have made actual comparisons of performance from the different commercial spectrometers using the same samples and the same tests. We hope this has been informative to the reader. Please contact us for more details or specifications.

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## 6 Appendix (Statistical Description of Evaluation Methods)

### 6.1 Measuring Wavelength Accuracy

Verify the wavelength accuracy of the spectrophotometer using a suitable reference standard. For this test, repeat measurements of the same reference material are made by placing it in the sample beam and not mechanically moving the sample over a normal measurement cycle for the instrument. For example, a 30 second measurement period, and 15 second reference spectrum may be typical. Then calculate the absorbance peak positions near the reference Wavelength position ( $\lambda_{ref}$ ) specified. The spectrum is measured for each scan (i.e., scan-to-scan for each sample) and for the mean spectrum over the full 30 second measurement period. Then the standard deviation of difference of the wavelength positions is computed for scan-to-scan readings within (n) replicate samples, and the mean spectrum position ( $\bar{\lambda}_i$ ) for the measured ( $\lambda_{ij}$ ) versus reference ( $\lambda_{ref}$ ) wavelength values. The standard deviation ( $s_i$ ) is calculated as:

$$s_i = \sqrt{\frac{\sum_{j=1}^n (\lambda_{ij} - \lambda_{ref})^2}{n}} \quad [1]$$

The mean difference for wavelength accuracy is determined by:

$$\text{Wavelength Accuracy (as mean difference)} = \bar{\lambda}_i - \lambda_{ref} \quad [2]$$

Where ( $\bar{\lambda}_i$ ) is the average wavelength for the scan-to-scan set; and ( $\lambda_{ref}$ ) is the reference wavelength position for the reference standard near the reference wavelength. The results are reported as: Wavelength (nm) precision and accuracy. This may be accomplished for multiple wavelengths depending upon the standard reference material measured.

	Nominal Reference Value ( $\lambda_{ref}$ )	Precision (scan-to-scan standard deviation from reference, Eq. 1)	Accuracy (as mean difference from reference, Eq. 2)
	<i>Reference</i>	Equation 1	Equation 2
Scan-to-Scan	-----		
Average	-----		

## 6.2 Measuring Wavelength Repeatability (Precision)

Verify the wavelength repeatability of the spectrophotometer using a suitable reference standard. For this test, repeat measurements of the same reference material are made. Then the peak position for each scan is recorded and the mean spectrum wavelength position ( $\bar{\lambda}_i$ ) is computed for all the measured spectra ( $\lambda_{ij}$ ). The standard deviation for wavelength is calculated as:

$$s_i = \sqrt{\frac{\sum_{j=1}^n (\lambda_{ij} - \bar{\lambda}_i)^2}{n-1}} \quad [3]$$

Where ( $s_i$ ) is the standard deviation for the scan-to-scan wavelength precision or repeatability for scan-to-scan measurements, and where ( $\lambda_{ij}$ ) are individual wavelength shifts of the peak positions for sample i and scan number j; ( $\bar{\lambda}_i$ ) is the average value for the scan-to-scan set; (n) is the number of replicate measurements (pool all scan-to-scan data).

The mean spectrum wavelength position ( $\bar{\lambda}_i$ ) is calculated as:

$$\bar{\lambda}_i = \frac{\sum \lambda_i}{n} \quad [4]$$

The results are reported as: Wavelength (nm) Precision/Repeatability

	Mean wavelength ( $\bar{\lambda}_i$ )	Precision/Repeatability ( $s_i$ )
	Equation 4	Equation 3
Scan-to-Scan		

### 6.3 Measuring the Absorbance or Photometric Accuracy

The photometric response accuracy of the spectrophotometer is measured using a suitable reference standard, with known absorbance units (AU) of approximately 100% reflectance (0.0 AU). This reference standard must be provided with reference measurements of at least two separated wavelength positions, for example, 1640 nm (*ref01*) and 2300 nm (*ref02*).

For this test, repeat measurements of the same photometric standard are recorded. The absorbance units (Au) are computed for the entire spectrum and specifically at the two measured reference wavelength points (*ref01* and *ref02*). The reference absorbance units for each wavelength position ( $A_{ref01}$  and  $A_{ref02}$ ) are measured for each scan for each sample ( $n$ ) at each wavelength location. The photometric accuracy statistics are calculated as:

$$s_{ref01} = \sqrt{\frac{\sum_{j=1}^n (A_{ij} - A_{ref01})^2}{n}} \quad \text{and} \quad s_{ref02} = \sqrt{\frac{\sum_{j=1}^n (A_{ij} - A_{ref02})^2}{n}} \quad [5a \ \& \ 5b]$$

Where ( $s_{ref\#}$ ) is the standard deviation (precision) for the scan-to-scan absorbance units at a specified wavelength # (nm) for the set of measurements, and where ( $A_{ij}$ ) are individual measurements of the absorbance units for sample  $i$  through scan-to-scan replicate measurement number  $j$ ; ( $A_{ref\#}$ ) are the actual reference values for the reference material at each of the measured wavelengths; and  $n$  is the replicate measurement number. (Remember to pool all scan-to-scan data.)

The mean difference for photometric accuracy at each wavelength position is determined by:

$$\text{Photometric Accuracy (as mean difference)} = \bar{A}_{ij} - A_{ref\#} \quad [6]$$

Where ( $\bar{A}_{ij}$ ) is the average measured photometric value at each of the selected wavelengths; and ( $A_{ref\#}$ ) is the known photometric reference value for the reference sample at a specific

wavelength. The results are reported as: Absorbance/Response (Photometric) Accuracy (in AU).

These can be computed for multiple calibrated wavelength positions if desired.

	Nominal Reference Value ( $A_{ref01}$ )	Precision ( $s_{ref01}$ )	Accuracy (as mean difference) $ref01$	Nominal Reference Value ( $A_{ref02}$ )	Precision ( $s_{ref02}$ )	Accuracy (as mean difference) $ref02$
	Reference	Equation 5a	Equation 6	Reference	Equation 5b	Equation 6
Scan-to-Scan	-----	-----		-----	-----	
Average	Same		-----	Same		-----

### 6.4 Measuring the Absorbance or Photometric Repeatability

The photometric repeatability of a spectrophotometer is measured using a suitable standard, for example a pre-specified reference sample with known or nominal absorbance unit (AU) values given for each wavelength measured.

For this test, repeat measurements of the same photometric standard are recorded. The measured absorbance units are determined for the entire spectrum and specifically at the two measured reference points, for example, 1640 nm ( $ref01$ ) and 2222 nm ( $ref02$ ). The absorbance units are measured for each scan (i.e., scan-to-scan for each sample) at the specific wavelengths of interest. The mean and standard deviation are computed at the two wavelength positions for scan-to-scan (within replicate samples). This statistic is calculated for both wavelengths as:

$$s_i = \sqrt{\frac{\sum_{j=1}^n (A_{ij} - \bar{A}_i)^2}{n-1}} \quad [7]$$

Where ( $s_i$ ) is the standard deviation for the scan-to-scan absorbance units (AU) repeatability for the scan-to-scan measurements, and where ( $A_{ij}$ ) are individual measurements of the absorbance for sample i and scan-to-scan number j; ( $\bar{A}_i$ ) are the mean measured values for the reference sample at each of the test wavelengths; n is the replicate number of spectra (pool all scan-to-scan data).



The mean spectrum photometric value ( $\bar{A}_i$ ) is calculated as:

$$\bar{A}_i = \frac{\sum_{i=1}^n A_i}{n} \quad [8]$$

The results are reported as follows. This can be repeated using a different calibrated set of wavelengths as needed.

Absorbance/Response (Photometric) Repeatability (in AU)

	Mean at ref01 ( $\bar{A}_i$ )	Repeatability ( $s_{ref01}$ )	Mean at ref02 ( $\bar{A}_i$ )	Repeatability ( $s_{ref02}$ )
	Equation 8	Equation 7	Equation 8	Equation 7
Scan-to-Scan				

## 6.5 Measuring the Photometric linearity

The photometric linearity of the spectrophotometer is measured by using a set of reference reflectance standards. The observed response ( $y$ ) is plotted against the expected response ( $x$ ). The slope of the line for reference ( $x$ ) versus measured ( $y$ ) data should be  $1.00 \pm 0.05$  and the intercept  $0.00 \pm 0.05$ . The slope and intercept are calculated using the reference material measurements absorbance (Au).

The results are reported as a graph of the measured linear response against the expected response at the two measured wavelengths, for example, 1640 nm (*ref01*) and 2300 nm (*ref02*). Record full spectral data; and include the following table: Linearity at 1640 nm and 2300 nm. Other wavelengths may additionally be selected as needed.

Slope at 1640 nm	Intercept at 1640 nm	Slope at 2300 nm	Intercept at 2300 nm
Equation 9a	Equation 9b	Equation 9a	Equation 9b

Note the slope ( $b$ ) and intercept ( $a$ ) for the data set of  $x_i$  (actual) and  $y_i$  (measured) pairs of measurements for each wavelength position is given as:

$$b = \frac{\sum_i \{(x_i - \bar{x})(y_i - \bar{y})\}}{\sum_i (x_i - \bar{x})^2} \quad \text{and} \quad a = \bar{y} - b\bar{x} \quad [9a \ \& \ 9b]$$

## 6.6 Measuring the Photometric Noise

To measure the photometric noise a reference reflectance standard at 0.0 AU (100% R or T) is used. Measurements of the reference standard are repeated and the sample is not moved during measurement. The photometric noise, peak-to-peak, is computed over the entire spectrum as the standard deviation of the spectrum over the measurement region. The photometric noise is computed as the standard deviation of the spectral response. This statistic is calculated for a single spectrum averaged over a standard measurement period as:

$$s_i = \sqrt{\frac{\sum_{j=1}^n (A_{ij} - \bar{A}_i)^2}{n-1}} \quad [10]$$

Where ( $s_i$ ) is the standard deviation (noise) for the *averaged* spectrum comprised of a number of scan-to-scan measurements for each wavelength over a specified number of scans, and where ( $A_{ij}$ ) are individual absorbance measurements  $i$  for the averaged spectrum at wavelength  $j$ ; ( $\bar{A}_i$ ) is the average absorbance units value for the averaged spectrum; and  $n$  is the number of data points (in wavenumbers). The mean spectrum photometric value ( $\bar{A}_i$ ) is calculated as Equation 8. This can be reported at one or more wavenumbers or over the entire measurement region.

The results are reported as: Photometric Noise

	Mean ( $\bar{A}_i$ )	Photometric Noise ( $s_i$ )
	Equation 8	Equation 10
Averaged Spectrum		

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