

Stray Light – Measurement and Effect on Performance in UV-Visible Spectrophotometry

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Introduction

Stray Radiant Energy (SRE) or stray light is the measured quantity of light that reaches the detector that is of a wavelength other than that selected. Therefore, stray light causes the measured transmittance to be erroneously high.

While a precise measurement of the total stray light present in a spectrophotometer is tedious, the fraction of stray light in a spectrophotometer is easily evaluated.¹ Stray light can be monitored using stray light cut-off filters to ensure stray light is not affecting absorption measurements on a given sample. These stray light measurements use Thermo Scientific certified reference materials.

This application note details the measurement stray light and its effects on UV-Visible spectrophotometry. This note does not discuss stray light in the optical system due to light leaks in the spectrophotometer. These leaks are not common in modern instruments and can be evaluated by simply covering the instrument with a dark cloth and verifying the measurements.

Theory

There are two types of stray light, monochromator stray light and instrumental stray light. In all spectrophotometers, light of a wide range of wavelengths enters the monochromator from the source, but only a very narrow band of wavelengths emerges from the exit slit. No monochromator is 100% efficient, and scattering and diffraction inside the monochromator introduce some radiation surrounding the desired wavelength. The stray light that results from the inefficiency of the monochromator is called monochromator stray light and is defined as¹

$$\text{Monochromator Stray Light} = \frac{\text{Radiation at unwanted wavelengths}}{\text{Total amount of radiation transmitted by the monochromator}}$$

The remainder of the optical system and the sample itself both modify the desired light from the monochromator and the total stray light. The detector cannot differentiate between photons of “correct” monochromatic radiation absorbed by the sample and stray light photons. Thus, signal produced by the detector is a combination of the effects of the absorbed light and the stray light. The combined effect of the monochromator stray light and stray light from other sources is called the instrumental stray light, and is defined as¹

$$\text{Instrumental Stray Light} = \frac{\text{Detector signal for all wavelengths outside the monochromator passband}}{\text{Total signal at a defined wavelength setting}}$$

Instrumental stray light determines the total effect of stray light on the absorbance reading.

Stray light manifests itself as an apparent deviation in the Beer-Lambert Law.² This effect is more obvious at higher concentrations of analyte because the stray light component becomes a larger fraction of the total transmitted light. Consider the following example where $T_{measured}$ is the measured transmittance, T is the ideal transmittance in the absence of stray light, and r is the stray light fraction.

$$T_{measured} = T + r$$

Converting this to absorbance, we have the following relationship, where the measured absorbance ($A_{measured}$) is defined as:

$$A_{measured} = -\log(T + r)$$

Figure 1 gives calibration plots with different amounts of stray light present. Notice that as the instrumental stray light increases, the effect on the linearity of the calibration curve becomes more dramatic, thus decreasing the linear working range of the instrument.

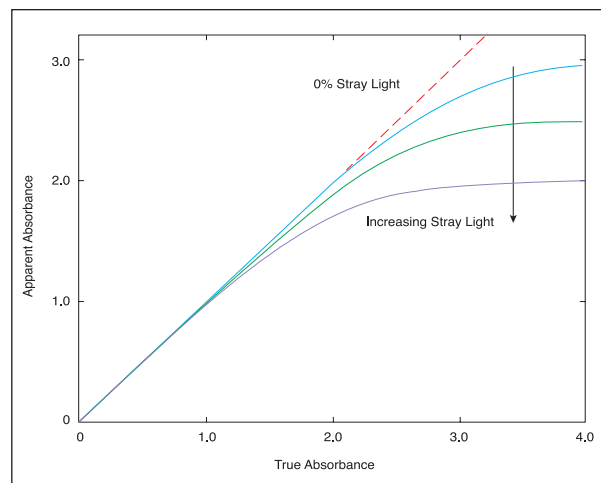


Figure 1: A plot of the apparent absorbance against the true absorbance with increasing stray light. The deviation from the Beer-Lambert law increases with increasing stray light.

Monitoring Stray Light

Quantifying the monochromator stray light in a spectrophotometer is an extremely tedious process requiring calibrated light sources and other specialized test equipment. Fortunately, it is quite easy to monitor the instrumental stray light, especially in the wavelength range where it has the most affect, the ultraviolet. The most convenient method of measuring stray light is with cut-off filters.

Key Words

- Evolution
- Glass Cut-off Filters
- Performance Verification
- Stray Light
- Stray Light Filters
- Spectronic Helios
- Spectrophotometer
- UV-Visible

A cut-off filter contains material that does not transmit radiation below a well-defined wavelength known as the cut-off wavelength. The absorbance of the filter rises sharply in the narrow wavelength range near the cut-off wavelength. The functionality of a cut-off filter is illustrated in Figure 2.

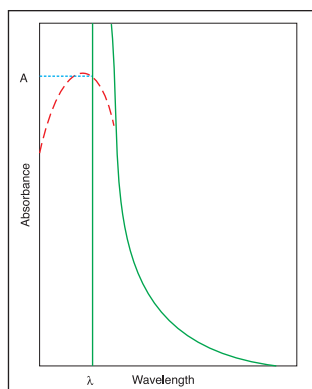


Figure 2: The functionality of a stray light cut-off filter. The absorbance of the filter material is represented as the solid line. The dotted line represents the apparent absorption curve. The apparent absorbance at wavelength λ is due to stray light.

Stray light should only be measured at a wavelength just beyond the filter; otherwise, a portion of the stray light would be absorbed by the filter. This would lead to an erroneously high absorbance that does not accurately represent the stray light present in the instrument. Therefore, stray light filters must be selected appropriately for the measurement wavelength. For example, sodium iodide solution is best to measure stray light at 220 nm. A complete list of stray light cut off filter certified reference materials is given in Table 1.

It is important to remember that instrumental stray light is a function of the “sample”, which includes the cell, the solvent, and the solute. Thus, a stray light measurement with a cut-off filter does not necessarily guarantee that the same level of stray light will be present when a sample is in the beam. However, the cut-off filters are excellent for determining the performance of the spectrophotometer and monitoring instrument performance over time.

Reference Solutions

Sealed solutions are the best filters for monitoring stray light in a UV-Visible spectrophotometer. Using sealed solutions eliminates the need to prepare solutions on a routine basis, as these solutions have a very limited shelf life under ambient conditions. Using sealed certified reference materials also eliminates any human error in the preparation process. Our certified reference materials are prepared according to the ASTM E-387 procedure using the highest quality reagents and sealed by heat fusion in a far-UV quartz cuvette. Each set of stray light solution set is supplied with a water blank cuvette for use as a reference.

Table 1 details the sealed reference solutions available from Thermo Scientific, as well as the appropriate cut-off wavelengths. The absorption spectrum of the individual stray light filters is given in Figure 3.

Part Number	Description	Cut-off Wavelength
9423UV95520E	Potassium Chloride Stray Light Filter	200 nm
9423UV95500E	Sodium Iodide Stray Light Filter	220 nm
222-216500	Sodium Nitrite Stray Light Filter	340 nm

Table 1: Sealed stray light filter solutions available from Thermo

Use of Glass Cut-off Filters

Glass cut-off filters provide an alternative to solutions for the detection of stray light at some wavelengths. Our instrument performance verification accessories use cut-off filters to verify that the stray light performance of the instrument is within specification at 220 nm and 340 nm. These automated tests enable the user to monitor any changes in stray light performance with time.

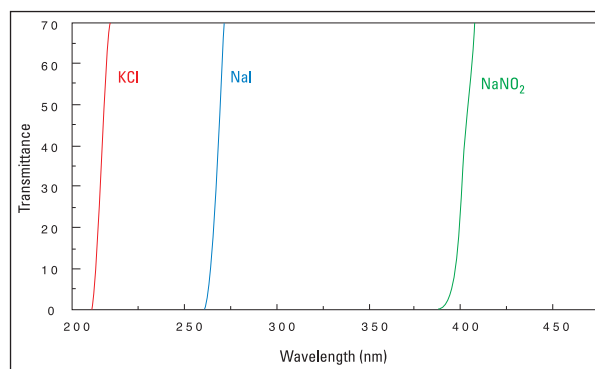


Figure 3: Transmission curves of the stray light cut-off filters offered by Thermo Scientific

Part Number	Description	Certification
9423UV61400E	Calibration Validation Carousel (CVC) for Helios™ Alpha and Beta spectrophotometers	National Physical Laboratory (NPL)
9423UV61460E	Calibration Validation Carousel (CVC) for Helios Alpha and Beta spectrophotometers	National Institute of Standards and Technology (NIST)
10010621	Smart Calibration Validation Carousel Accessory for Evolution™ 300 and Evolution 600 spectrophotometers	NPL
10010721	Smart Calibration Validation Carousel Accessory for Evolution 300 and Evolution 600 spectrophotometers	NIST
10010601	CVC Carousel Only for Evolution 300 and Evolution 600 spectrophotometers	NPL
10010701	CVC Carousel Only for Evolution 300 and Evolution 600 spectrophotometers	NIST

References

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- Ingle, James D., Jr.; Crouch, Stanley R. *Spectrochemical Analysis*. Prentice Hall, New Jersey, 1988.

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