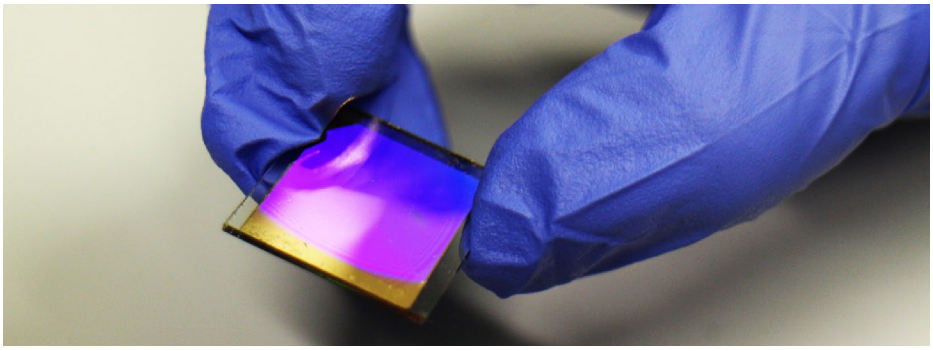
Technical Overview

Effects of Filter Composition, Spectral Bandwidth, and Pathlength on Stray Light Levels in the Near-Infrared Region

Evaluating stray light levels on the Agilent Cary 5000/7000 UV-Vis-NIR spectrophotometers



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Abstract

Stray light quantification is an important aspect in evaluating spectrophotometer performance, as it can affect the accuracy of quantitative measurements. Stray light is defined as the light detected from wavelengths outside the specified wavelength reaching the detector.

Stray light levels on the Agilent Cary 5000 UV-Vis-NIR and Agilent 7000 Universal Measurement Spectrophotometer (UMS) are normally measured using chloroform ($CHCl_3$ at 2,365 nm) and water (H_2O at 1,420 nm) filters in the infrared region. As part of the introduction of the new PbS detector to the Cary 5000/7000 spectrophotometers that is under PbSmart control, a new stray light sample can now be used. Dibromomethane (CH_2Br_2 at 1,690 nm) is a liquid based optical filter that is suitable for assessing stray light levels in the near-infrared (NIR) region.

The influence of filter composition, pathlength, and bandwidth on the results of the stray light test in the NIR region of a spectrophotometer was evaluated by measuring dibromomethane, chloroform, and water filters.

Introduction

Stray light is a source of inaccuracy in spectrophotometry—specifically radiation that exits the monochromator at wavelengths outside the desired bandwidth for a given wavelength. Increased stray light levels can be caused by imperfections in the optical elements of the spectrophotometer, diffraction effects, or from contaminated internal components. Stray light can also be generated from light that is external to the spectrophotometer. For example, light from the laboratory can leak into the sample compartment or through another entry point.

When illuminated, the detector inside the instrument does not differentiate between the sources of the light that it measures. All incident light is measured. Measured stray light has two components. Light from the source in the instrument that lies outside of the bandwidth and wavelength of interest, and ambient light that reaches the detector either directly or by simple reflections.

Stray light can affect the linear relationship between measured absorbance and concentration, especially at higher absorbances. It introduces a systematic bias that reduces the measured absorbance values at high concentrations (Figure 1), leading to inaccuracies and errors in the quantitative data. These errors are due to the stray light that decreases photometric selectivity and creates a nonlinear photometric response (degradation of the Beer-Lambert law).

This technical overview explores how stray light measurements are affected by filter type and methodology, as well as the causes of stray light errors due to instrument-based imperfections. The influence of filter composition, use of rear beam attenuation, pathlength, and bandwidth on the results of the stray-light test in the NIR region of a spectrophotometer was examined. An Agilent Cary 5000 UV-Vis-NIR spectrophotometer was used in the study, but the findings are also relevant to the Agilent 7000 Universal Measurement Spectrophotometer (Figure 2).

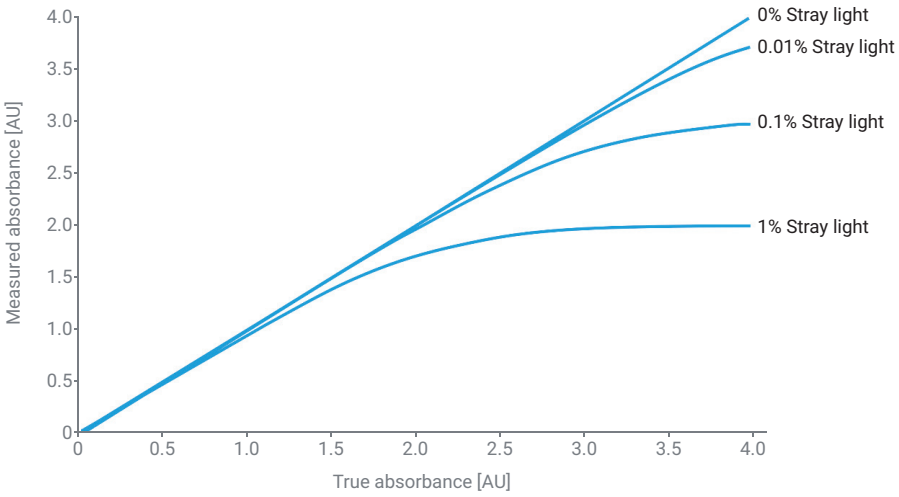

Figure 1. The effect of stray light on measured sample absorbance.

Figure 2. The Agilent Cary 7000 UV-Vis-NIR Universal Measurement Spectrophotometer.

Best filter composition to quantify stray light

To measure stray light, a filter is needed. Ideally, the filter would absorb all light of the wavelength at which the measurement is to be performed and transmit higher and lower wavelengths (Figure 3). When measuring transmittance (T) at the 0%T point of this ideal filter, any light detected would be a measure of stray light in the system.

In practice, however, such a filter does not exist. Instead, cutoff filters are used that transmit light above or below a certain wavelength and block all light in the wavelength range of interest.

The stray light tests use liquid solutions that ideally have no transmission within a specified wavelength range, so that any light reaching the detector indicates the presence of stray light. Salt solutions such as potassium chloride (12 g/L), sodium iodide (10 g/L), and sodium nitrite (50 g/L) in water are used as standard stray-light filters at 198, 220, and 340 nm, respectively (Figure 4). To assess stray light levels in the NIR region, chloroform and water standards, which have a cutoff wavelength at approximately 2,365 and 1420 nm respectively, are typically used.

Instrument-based sources of stray light

Electromagnetic radiation at wavelengths other than the wavelength of interest interfere with the measured results. The radiation can originate from various places within the instrument:

- Light coming through gaps in the spectrophotometer's enclosure
- Light scattering from mechanical surfaces inside the system
- Imperfections on the optical surfaces, which may lead to scattered or diffracted light
- Contamination of the optical components in the monochromator, diffraction grating, and light scattering parts of the instrument.
- Poorly managed blackbody (heat radiation) inside the instrument
- Poor quality order sorting filters that are used at the entrance of the monochromator to block higher-order (shorter wavelength) reflections from the diffraction grating.

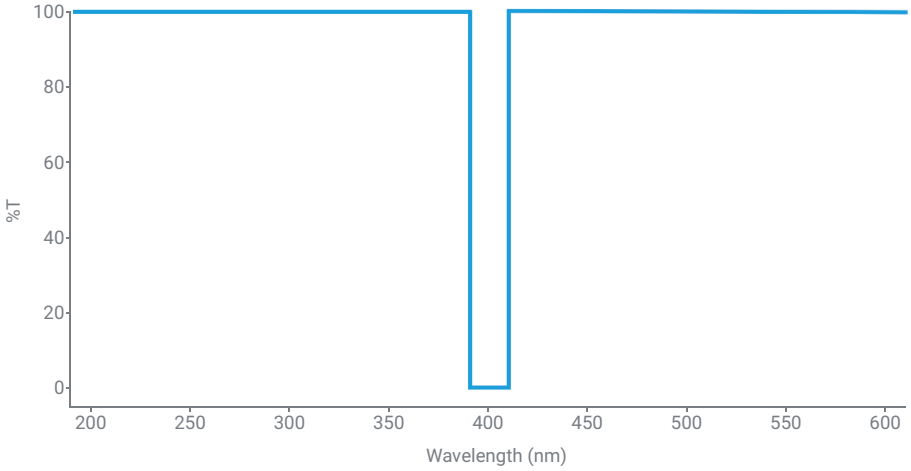

Figure 3. Ideal spectrum for a stray light filter.

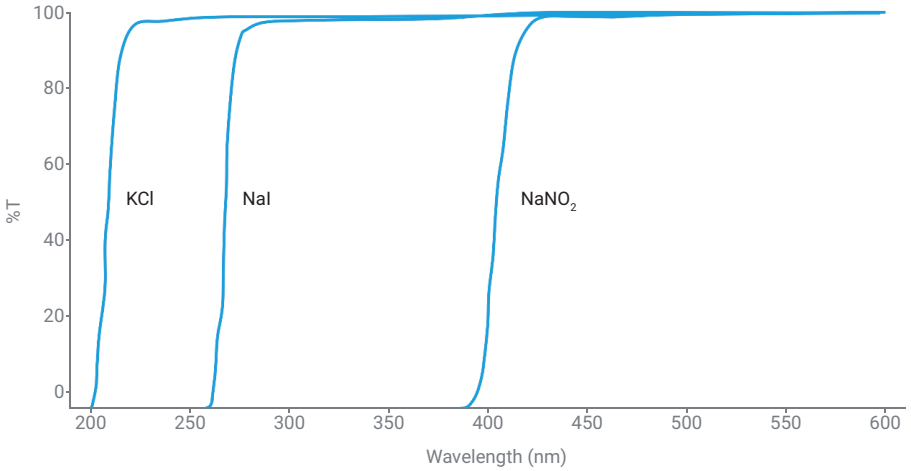

Figure 4. Spectra of potassium chloride (12 g/L), sodium iodide (10 g/L), and sodium nitrite (50 g/L) in water.

Experimental

Instrumentation

The stray light levels of the Cary 5000/7000 UV-Vis-NIR spectrophotometer in the NIR range were evaluated. The filter was dibromomethane (CH_2Br_2), which has a notch (high absorbance) wavelength at 1,690 nm (Sigma-Aldrich, CAS number 74-95-3). To measure stray light levels precisely, method parameters were varied, as listed in Table 1. The parameters included spectral bandwidth (SBW), signal averaging time (SAT), and pathlength. The spectra acquired for the dibromomethane filter around the specified wavelength of 1,690 nm at different pathlengths, resembled the ideal spectral profile for stray light measurements (Figure 3). The spectra confirmed the suitability of dibromomethane for stray light measurements in the NIR.

Chloroform and water stray light filters were also assessed in this study, using the parameters described in Table 1. Chloroform (Starna Scientific Ltd. - RM-$CHCl_3$) and water blank (H_2O) filters were used to calculate stray light levels at 2,365 and 1,420 nm, respectively.

Results and discussion

The influence of filter composition, SBW, and pathlength on stray light values were investigated. Initially, wavelength scans over the specified range for dibromomethane were performed using 10 and 50 mm pathlength cells (Table 1). The two pathlengths were scanned with different spectral bandwidths demonstrating the effect of SBW on stray light values for this filter.

To calculate stray light values, three measurements were needed: 100%T, 0%T, and the filter measurement. Once these values had been obtained, the following equation was applied to estimate stray light values:

Stray light %T = ((Filter %T – 0%T)/(100%T – 0%T)) × 100

Using a 10 mm cuvette and 2 Abs RBA, stray light values with dibromomethane at 1,690 nm were found to be 4.08E-04, 5.48E-04, 1.17E-02, 3.40E-01, and 3.28E+00 %T with 6, 8, 12, 16, and 20 nm SBW, respectively.

Low stray light levels and sharper peaks were observed with narrower SBW as shown in Figure 5. Upon increasing the SBW from 6 to 20 nm, broader peaks were observed, as expected. Increasing the SBW allows more stray light to get through from the edges of the peak, lowering the Abs levels (higher %T).

Using a 50 mm cuvette and 2 Abs RBA, stray light values with dibromomethane at 1,690 nm were found to be 2.06E-04, 1.83E-04, –9.20E-05, –7.70E-05, and 5.73E-04 %T with 6, 8, 12, 16, and 20 nm SBW, respectively. Negative stray light values indicate reaching the detection limit (noise floor) of the instrument as shown in Figures 5 and 6. Negative stray light values can be avoided using longer SAT.

Table 1. Parameters used to evaluate stray light levels on the Agilent Cary 5000/7000 UV-Vis-NIR spectrophotometer using dibromomethane, chloroform, and water filters.

Parameter	Dibromomethane (CH_2Br_2)	Chloroform ($CHCl_3$)	Water (H_2O)
Wavelength Range (nm)	1,660 to 1,720	2,345 to 2,385	1,380 to 1,440
Signal Averaging Time (s)	1	1	1
Data Interval (nm)	1	1	1
Spectral Bandwidth (nm)	6, 8, 12, 16, and 20 (Fixed)	Auto	Auto
Rear Beam Attenuation (RBA)	2 Abs mesh filter	3 Abs mesh filter	3 Abs mesh filter
Cuvette	Quartz	Quartz	Quartz
Pathlength (mm)	10 and 50	10	10

Low stray light levels were measured using water (1,420 nm) and chloroform (2,365 nm) filters in a 10 mm cuvette and 3 Abs RBA. The stray light values were 3.50E-05 and 2.13E-04 %T, respectively, as shown in Figure 7.

Figure 6 shows the transmission approaches the system's stray light limit at an SBW of ±15 nm of the central wavelength of 1,690 nm using the 50 mm pathlength. Therefore, an SBW of 10 to 15 nm can be used without the edges of the absorbance peak affecting the peak value. With the 10 mm pathlength (Figure 5), the range is ±7 nm, meaning that a narrower SBW must be selected, which will result in a lower signal-to-noise ratio (SNR) or a longer measurement time.

Using a relevant pathlength and spectral bandwidth while avoiding saturation of the detector or under estimation of stray light is important. Signal averaging time should be adjusted according to instrument performance to obtain low noise (avoiding negative %T values) and precise stray light values.

In selection of a suitable method to estimate stray light levels, repeatability of results that are not affected by noise and measurement time should be the main selection criteria. Stray light values for dibromomethane obtained for different settings are summarized in Table 2.

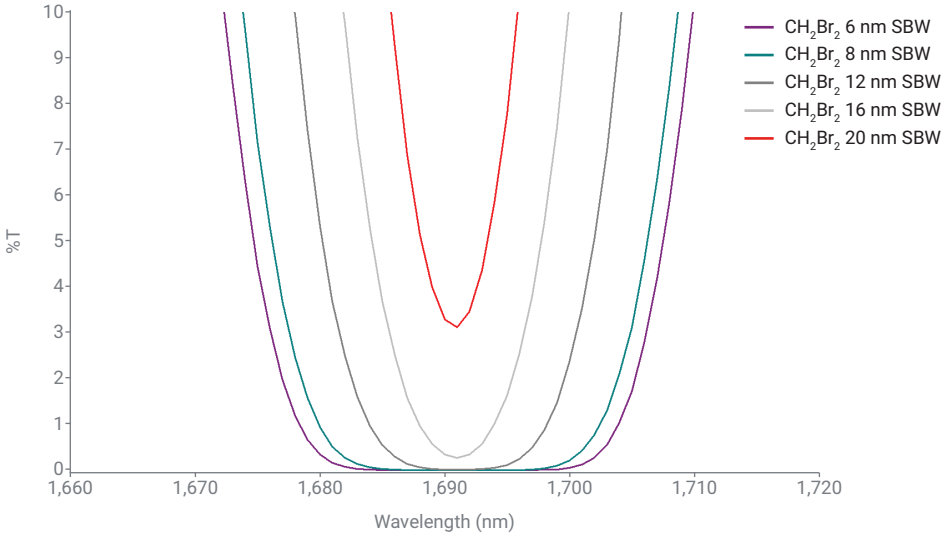

Figure 5. Spectra of dibromomethane using a 10 mm cuvette with 2 Abs RBA and varying SBW (6, 8, 12, 16, and 20 nm).

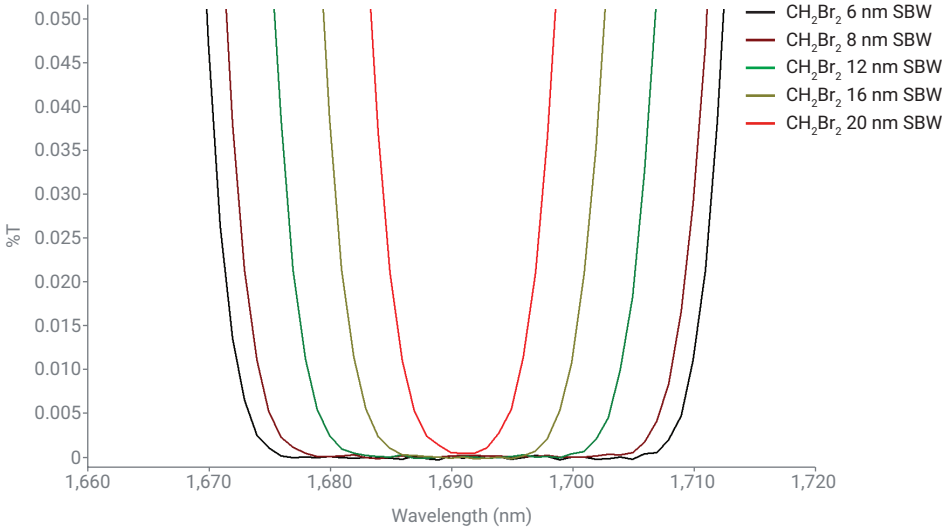

Figure 6. Dibromomethane spectra using a 50 mm cuvette with 2 Abs RBA and varying SBW (6, 8, 12, 16, and 20 nm).

Table 2. Stray light values for dibromomethane obtained using different settings.

Entry	Pathlength (mm)	Rear Beam Attenuation	Spectral Bandwidth (nm)	Wavelength (nm)	Stray Light (%T)	Stray Light (Abs)
1	10	2 Abs	6	1,690	4.08E-04	5.38
2	10	2 Abs	8	1,690	5.48E-04	5.26
3	10	2 Abs	12	1,690	1.17E-02	3.93
4	10	2 Abs	16	1,690	3.40E-01	2.46
5	10	2 Abs	20	1,690	3.28E+00	1.48
6	50	2 Abs	6	1,690	2.06E-04	5.68
7	50	2 Abs	8	1,690	1.83E-04	5.73
8	50	2 Abs	12	1,690	−9.20E-05	NA
9	50	2 Abs	16	1,690	−7.70E-05	NA
10	50	2 Abs	20	1,690	5.73E-04	5.24

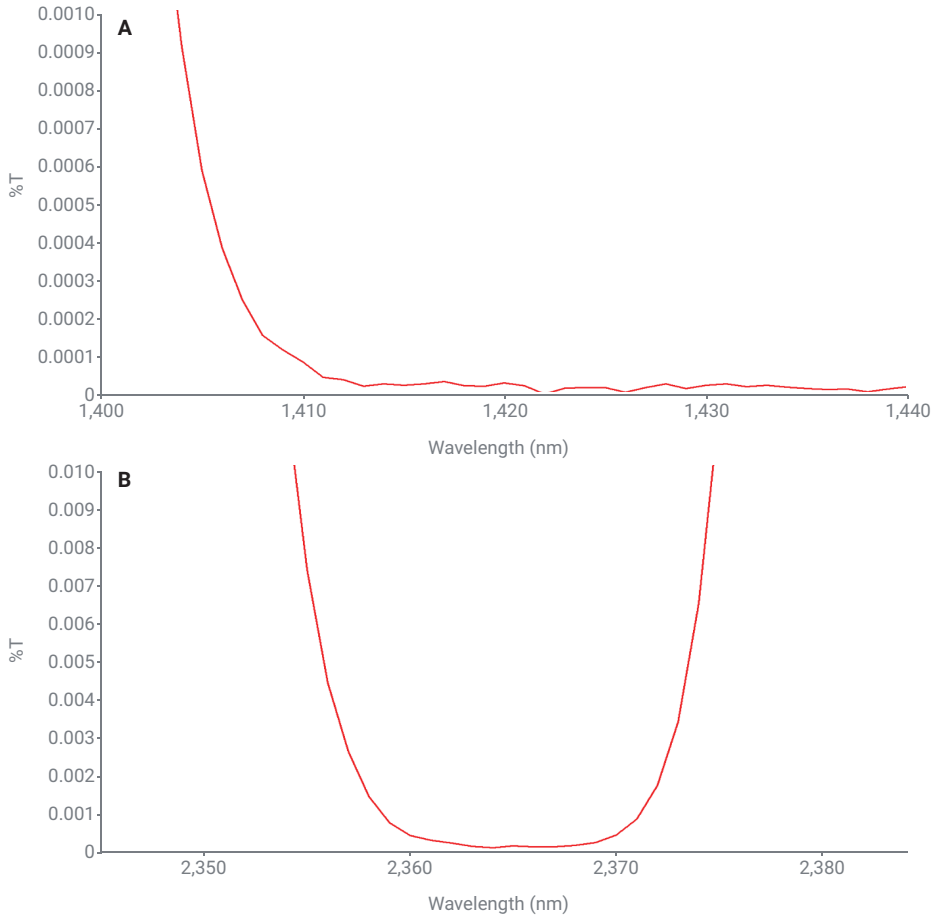

Figure 7. NIR stray light filter spectra measured on the Agilent Cary 5000/7000 using a 10 mm cuvette, 3 Abs RBA, and auto SBW; (A) water (1420 nm); (B) chloroform (2365 nm).

Conclusion

Many factors have been shown to influence the measured stray light values of a UV-Vis-NIR spectrophotometer. These factors include pathlength, spectral bandwidth, filter composition, and instrument imperfections. High stray light levels can lead to decreased absorbance readings, changes in spectral band shape, and ultimately the maximum absorbance that is measurable by the instrument.

The Agilent Cary 5000/7000 spectrophotometers showed low stray light levels in the NIR region when evaluated using dibromomethane, chloroform, and water filters. Low stray light levels ensure high quality and accurate results even for challenging samples such as those with a high optical density (OD).

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