Estimation of Stray Light using Starna Certified Reference Materials (CRMs)

Purpose

Use of liquid 'Cut-off' filters to qualify the Stray Light (or Stray Radiant Energy) of ultraviolet spectrometers.

Chronology

Stray Light has been simply described by Burgess as 'radiant energy to which the detector is sensitive, and which should not be there'. This effect had been observed as an underestimation of high absorbances, and discussed at length as early as 1948 when the leading spectroscopists of the time debated the performance limitations of the new Beckman Model DU. It would appear that these scientists did not take the 'black-box' approach to data that was being generated, no pun intended.

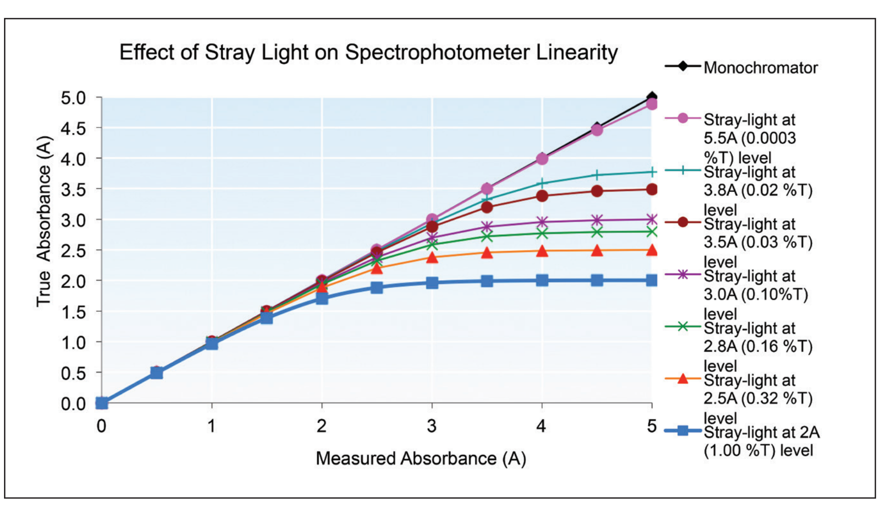
In 1969 ASTM (now ASTM International) published E387 – 'Estimating Stray Radiant Power Ratio of Dispersive Spectrophotometers by the Opaque Filter Method' [1]. This standard, updated on a periodical basis, has remained the 'de-facto' standard by which the Stray-Light performance of most modern spectrophotometers is estimated, and is discussed below. In 1982, Melienz, et. al. [2], defined Stray-Light as 'spurious radiant energy that has departed from its regular path in a spectrophotometer and then re-enters the path so that it is sensed by the detector and causes false readings of transmittance and absorbance.' and offered a refinement on the estimation method in current use at the time, and which has since been incorporated into E387, and USP General Chapter <857> [3].

Description

A range of liquid cut-off filters that allow Stray Light to be checked at a range of wavelengths from 200 nm to 390 nm. Starna liquid Stray Light references are supplied permanently sealed by heat fusion into either 5 mm or 10 mm high quality far UV quartz cells. Starna Stray Light Certified Reference Materials are prepared in accordance with ASTM E-387, and USP General Chapter <857>.

In both of these reference standards the method of 'best practice' uses the combination of 5 mm and 10 mm, by methodology proposed by K. Melienz (NIST) in 1982, defined in E-387 as the Solution Filter Ratio method, or more generally known as the 'Melienz' method.

Stray Light, also called Stray Radiant Energy or Power, is any light reaching the detector that is outside the Spectral Band Width selected for analysis by the monochromator. It can be due to optical imperfections or stray reflections within the monochromator itself or to light leaks or other effects in the rest of the optical system. As the detector cannot discriminate between the analytical wavelength and the Stray Light, the Stray Light contributes to the detector signal and introduces an error in the measured absorption. The Stray Light is not absorbed even at high concentrations of the absorbing species, so its effect is a negative deviation from the linear relationship between concentration and absorbance (the Beer-Lambert law) on which most quantitative determinations are based.



Stray light is wavelength and instrument dependant. It can be present at any wavelength but is most noticeable when the energy throughput of the system at the analytical wavelength is relatively low, for example in the far UV region, and any Stray Light will be comparatively more significant. At these wavelengths, any deterioration in the instrument optics or UV light source will exaggerate the apparent Stray Light, so it is desirable to check it even if the instrument is not to be used in the far UV, as it is an excellent way of monitoring the condition of the instrument optical components.

The usual way of assessing Stray Light is to measure, at the desired analytical wavelength, a sample that totally absorbs the radiation at that wavelength, but transmits at all other wavelengths. Any light detected by the instrument is then Stray Light.

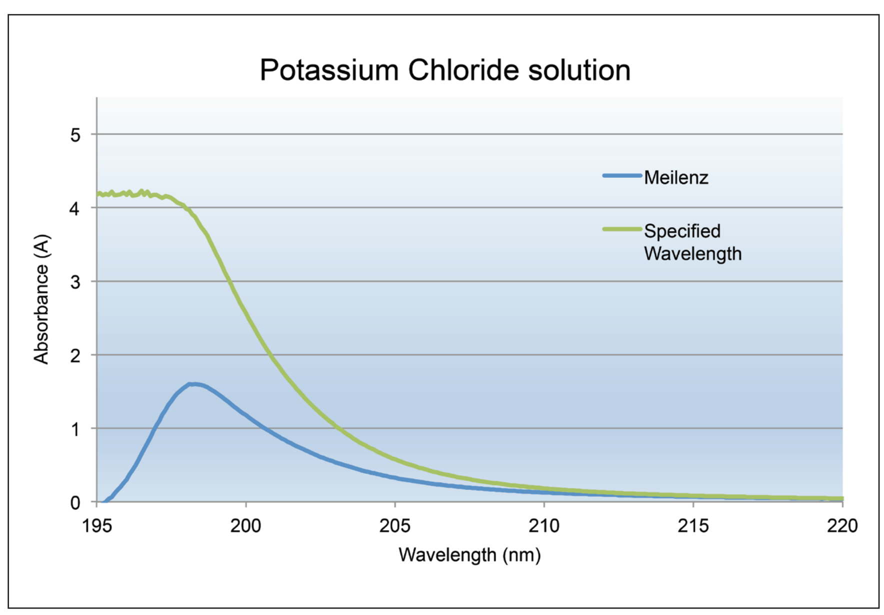
Practically, the usual method is to use cut-off filters or solutions that cut off all light near the analytical wavelength, and transmit at all higher wavelengths. Starna Stray Light CRMs have very sharp transitional (cut-off) spectra, giving excellent filtering characteristics.

Solution Filter Ratio Method (Mielenz)

In this method (proposed by Mielenz et. al.), the reference beam is attenuated by a 5 mm path length cuvette containing the same edge filter solution as used in a 10 mm path length cuvette placed in the sample beam. A maximum peak differential absorbance is observed (ΔA), whilst scanning through the edge absorbance, which is related empirically to the Stray-Light level by

$$s = 0.25 \times 10^{-2 * \Delta A}$$

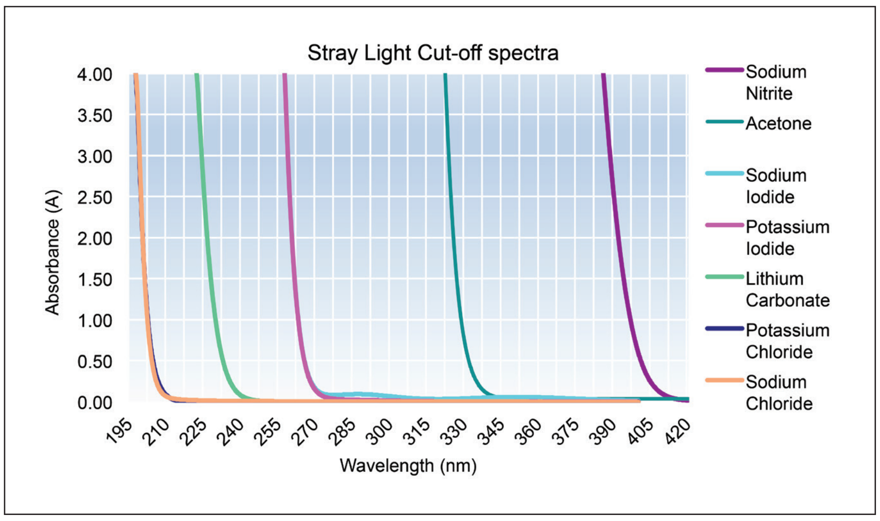
This method therefore avoids the somewhat awkward and potentially difficult procedure to find appropriate attenuation filters in the UV region required to 'back-off' the system, especially if using a modern double-monochromator spectrophotometer, and also a measurement performed at the limit of the instrumental range and A/D electronic resolution.



Specified Wavelength Method

In this method, if required, appropriate attenuating filters are measured at the required wavelength, are used to 'back-off' the spectrophotometer, in order to keep the apparent absorbance peak below the cut-off wavelength on scale. The estimated Stray-Light value is then simply the sum of the attenuator value(s), plus the measured peak value.

The certified wavelength is that at which the spectrum transitions 2.0 A. Below this wavelength, within the indicated usable range, any indication of light transmission must be Stray Light.



Material	Concentration	Cut-off	Usable Range
Sodium Nitrite	5% aqueous	391 nm	300 - 385 nm
Acetone	Spectroscopy grade	326 nm	250 - 320 nm
Potassium Iodide	1% aqueous	260 nm	210 - 259 nm
Sodium Iodide	1% aqueous	260 nm	210 - 259 nm
Lithium Carbonate	Saturated aqueous	227 nm	210 - 225 nm
Sodium Chloride	1% aqueous	201 nm	175 - 200 nm
Potassium Chloride	1.2% aqueous	201 nm	175 - 200 nm

Several of these filters are approved for instrument qualification by Pharmacopoeias and other standardisation bodies, and the table below shows one of these cited values, where the stated requirement is '…is greater than 2.0 @ 198 nm when compared with water as compensation liquid' [4].

Value comparison table

'Mielenz' Absorbance (A)	Specified Wavelength (s) Absorbance
0.3	1.2
0.5	1.6
0.7	2.0
1.0	2.6
1.5	3.6
2.0	4.6
2.5	5.6

References

1. ASTM International E387-04 (2014) – Standard Test Method for Estimating Stray Radiant Power Ratio of Dispersive Spectrophotometers by the Opaque Filter Method.

2. Melienz, K.D., Weidner, V.R. and Burke, R.W., Applied Optics, 1982, 21, 3354.

3. United States Pharmacopeia, "General Chapters, Ultraviolet-visible Spectroscopy", USP 38-NF33, <857>, (2015).

4. European Pharmacopoeia 8.0, 2.2.25, 40.

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The new Starna USP kits provide all the appropriate liquid reference materials, in a permanently heat-fused sealed format, so that the required parameter verification to specific instrumental requirements can easily be performed.

Between 2010 and 2015, the Spectroscopy sub-committee, of the General Chapters, Chemical Analysis Expert Committee of the United States Pharmacopeia (USP) was tasked to extensively revise and update the Spectroscopy <851> chapter.

The original chapter, whilst covering the general spectroscopic principles, did not provide sufficient guidance with respect to the specific, and discrete techniques in use in modern laboratories.

Therefore, the current revision has resulted in a suite of technique specific General Chapters, of which the Ultraviolet Visible Spectroscopy chapter <857> is one. These are to be implemented from 1 May 2015.

As a mandatory chapter, it details how the essential Qualification requirements regarding the key parameters of wavelength accuracy, photometric accuracy/linearity, Stray Light, and resolution, must be met on a UV-Visible spectrophotometer.

The New USP requirement to qualify the Stray Light and resolution characteristics, provide a significant degree of harmonisation with the requirements of the other major pharmacopoeias.

In addition, the Stray Light section in this chapter adopts the published protocols found in ASTM International standard E387 " Standard Test Method for Estimating Stray Radiant Power Ratio of Dispersive Spectrophotometers by the Opaque Filter Method ". This uses a combination of 5 mm and 10 mm path length cuvettes, filled with the same 'cut-off' solution.

All the new references are manufactured and calibrated by Starna Scientific; UKAS Accredited to both ISO Guide 34 (4001) as a Reference Material producer, and ISO 17025 (0659) as a Calibration Laboratory for optical reference measurements. Starna Scientific's manufacturing facility is also accredited to the ISO 9001 Quality Management System with BSI.

A Certificate of Calibration and Traceability and full instructions for use are provided with each Reference Material. The certificate is supplied in electronic format, on a USB drive in the same box as the references, allowing hard copy to be produced on demand and giving easy interface to the user's own IT systems. Certification measurements are made on a reference spectrophotometer that has been qualified using Standard Reference Materials certified by the National Institute of Standards and Technology (NIST) in the USA, or against primary physical references such as elemental emission lines.

Starna offers a Lifetime Guarantee on all Starna Certified Reference Materials, unless otherwise stated, such that any reference material that moves outside its published uncertainty budget will be replaced free of charge. This guarantee is subject to the reference materials being re-certified at least every two years by Starna and that the references have not been physically, thermally or optically abused. The Starna UKAS accredited calibration laboratory aims to re-certify and despatch references within five working days from receipt.

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