HORIBAJOBIN YVON

Instrument Response Corrections

Introduction

All devices for analyzing light, by their very nature, are wavelength dependent. Gratings, for example, are most efficient at their blaze angles and so deliver more light at the associated wavelengths. Detectors themselves are more responsive in some regions than in others. Lenses, beam splitters, windows, and other components all contribute to variations in observed intensity. These phenomena are often described collectively in terms of an instrument response curve, which traces the effect of an instrument system on intensity measurements as a function of wavelength.

Whenever it is crucial to define the precise shape of spectral features or intensity ratios of different peaks, instrument effects must be removed from the data. Corrected spectra are required, for example, to compare detector performance, determine the exact position of a laser mode, calculate a scattering cross section, or compute the quantum yield of a luminescent substance. Instrument corrections adjust the observed intensity value of each data point in a spectrum by a factor that represents the relative response of the instrument at that point.

Relative Corrections vs. Absolute Corrections

A relative instrument response correction is the one most commonly used. It gives the true relative peak intensities and corrects for all instrument properties on a relative basis. An absolute correction, however, allows the user to measure spectral data in absolute irradiance units from which absolute power levels can be calculated. Both types of corrections require the measurement of the instrument relative response function.

The relative response function for an instrument is defined as the ratio of the data obtained with the standard source or detector to the calibration data for the standard; i.e., the ratio of observed intensity to true intensity. The resulting curve is often normalized. In fact, any multiple of this curve represents the relative response of the instrument over the range of interest.

Multiplying spectroscopic data by the inverse of the relative response function yields accurate wavelength position and true relative intensity of spectral peaks; spectra corrected with different multiples of the function will differ only by a uniform vertical expansion factor. For most applications, a relative correction can be used. For relative corrections, a stable white
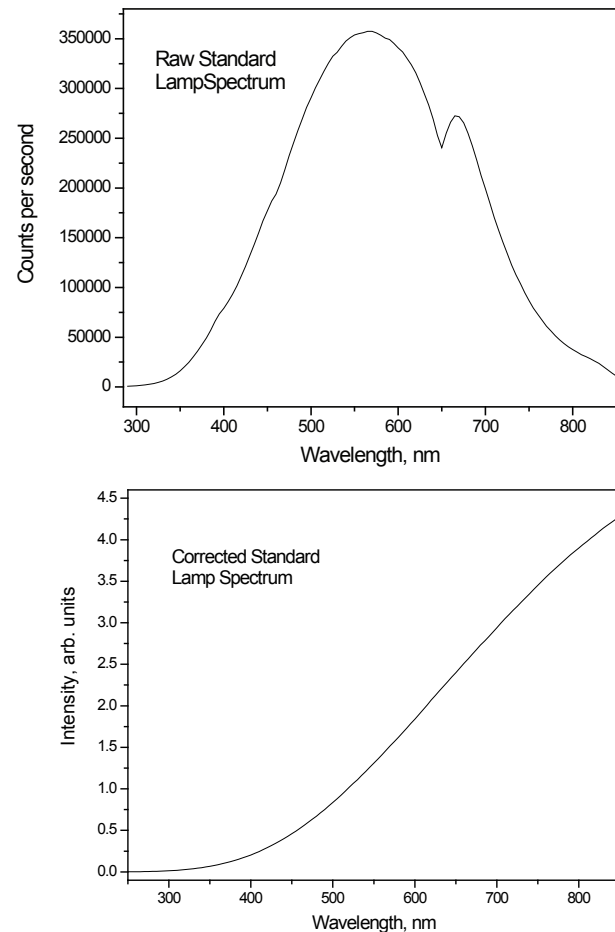

Figure 1. Measured spectrum (top) of standard tungsten lamp with a Triax550 spectrometer and a 1200 gr/mm x 500 nm grating using a PMT with photon counting. Corrected spectrum (bottom) of the same tungsten lamp.

light source such as a tungsten-halogen lamp or flashlight with tungsten bulb is sufficient, provided the spectral distribution of the source is known.

To calculate absolute corrections, also called Radiometric Corrections, it is only necessary to choose the factor that will yield the correct intensity value for a single known point on the curve. Radiometric corrections are required when performing an absolute quantum yield measurement, measuring the power from an LED or light source, or whenever a calibrated measurement is required. For radiometric corrections a light source traceable to NIST, such as Model 1908 quartz tungsten-halogen lamp and mounting assembly from HORIBA Jobin Yvon.

Establishing a Relative Correction File

The procedure to establish a correction file is essentially the same for both standard-source and standard-detector corrections. The outline of such a procedure follows.

1. **Instrument Setup**

   First, the standard light source or detector must be incorporated into the spectroscopic system. A standard lamp is mounted so that the output is diverted into the collection optics. The light is scattered from a plate that has been coated with a material known to have flat spectral characteristics (reflectance standard or integrating sphere) to ensure homogeneous illumination of the optics (the scattering plate is positioned at a designated distance from the entrance slit, to match the f/# cone of the spectrometer). Then, the spectrometer's collection optics collect the light and pass it through the system to the detector.

2. **Experiment Setup**

   The source employed for the determination should provide radiation over the spectral range of interest. All instrument parameters, including bandpass (slit widths), order-sorting filters, and wavelength increments should be set as they will be used for the actual experiment to be performed.

3. **Acquire a Spectrum**

   With the system configuration as described above, scan the spectrometer over the region of interest and store the resulting spectrum as data file "stdlamp." The measurement should be conducted under conditions which reproduce, as nearly as possible, the conditions under which experimental data will be acquired. Background noise should be subtracted from the recorded spectrum. This can be done by manually blocking the source, scanning dark data into another file, and then subtracting this file from the first. In some software packages it is possible to automate this process.

4. **Irradiance Units**

   Most standard lamps are calibrated in terms of energy as a function of wavelength, denoted $E(\lambda)$. Although this expression is standard in radiometry, other applications follow different unit conventions. For example, luminescence data are usually presented in counts/wavelength $(Q(\lambda))$ or counts/wavenumber $(Q(\upsilon))$. The relationships among the four standard unit forms can be expressed as:

$$Q(\upsilon) = \lambda E(\upsilon) = \lambda 2Q(w) = \lambda 3E(\lambda)$$
$$(\text{Eqn. 1})$$

where Q and E represent Quantum and Energy functions, respectively, and υ and λ stand for the units of wavenumber and wavelength, respectively. In practical terms, this means that when a photon-counting type of detector is used (such as PMT with a DM302 photon counting module or a CCD), each Y-value in the standard lamp irradiance dataset must be multiplied by the corresponding wavelength value or X-value. For photodiode detectors and PMT detectors operated in current or voltage mode, the standard lamp irradiance dataset is used without modification.

5. **Creating a Calibration File**

   Create a data file "Irr" with the same parameters as "stdlamp." For each data point in the file, enter the irradiance value of the calibrated standard as the Y-coordinate. The data points in this calibration curve must match those in the scan; i.e., they must begin and end at the same wavelength and have the same wavelength increment between data points. It may be necessary to interpolate values for the calibration curve in order to provide a more appropriate set of data points for the response function. In general, a system correction file is generated by taking a spectroscopic measurement of an Unknown (may be a lamp or sample) and dividing it by a Known (calibrated spectrum). For example, a correction file for a spectrometer system (here called the Instrument Response) can be generated as follows:

$$\text{Instrument Response} = \frac{\text{Measured spectrum of calibrated lamp}}{\text{Theoretical spectrum of lamp}}$$
$$(\text{Eqn. 2})$$

6. **Calculating the Correction File**

   To calculate a correction file, which is the inverse of the Instrument Response curve, divide the calibration file "Irr" by the data file "stdlamp." This will cause each value in the calibration curve to be divided by the corresponding value from the scan. Name the resulting file "mcorrect."

$$\text{mcorrect} = \frac{\text{IRR}}{\text{stdlamp}}$$
$$(\text{Eqn. 3})$$

Save this file as "mcorrect.spc." If desired the curve may be normalized by dividing by the minimum value of "mcorrect" and then saved as "mcorrect.spc." A typical "mcorrect" spectrum is shown in Figure 2. The file "mcorrect.spc" can be imported and used as a correction routine for application to experimental data.

Applying Corrections

Multiply the saved "mcorrect" spectrum (described in the previous section) by the raw spectral data measured during an actual experiment. In both the HORIBA Jobin Yvon software packages SynerJY® and FluorEssence®, the mcorrect.spc file can be loaded as a correction file, and will automatically multiply the raw data by the correction file. Other software packages may handle correction files differently, so the software manual should be consulted.

The differences between these raw and corrected spectra emphasize the importance of instrument response corrections of performance data used to make critical design or quality control decisions.

A correction file generated using the above procedures is valid under certain specified conditions, including lamp current and distance from the source to detector (here, distance from source to spectrometer entrance slit), and typically has an uncertainty value of ±5%. Absolute correction measurements are particularly sensitive to these conditions. Since calibrated lamps have a relatively short lifetime (typically maintain calibration for 50-100 hours) it is recommended to test the calibration procedure first using an uncalibrated light source, and when the user is comfortable with the procedures, to make sure all equipment is completely ready before turning on the calibrated light source.

> **NOTE:** Because dark counts are not wavelength dependent, a background spectrum should always be subtracted before instrument corrections are applied.
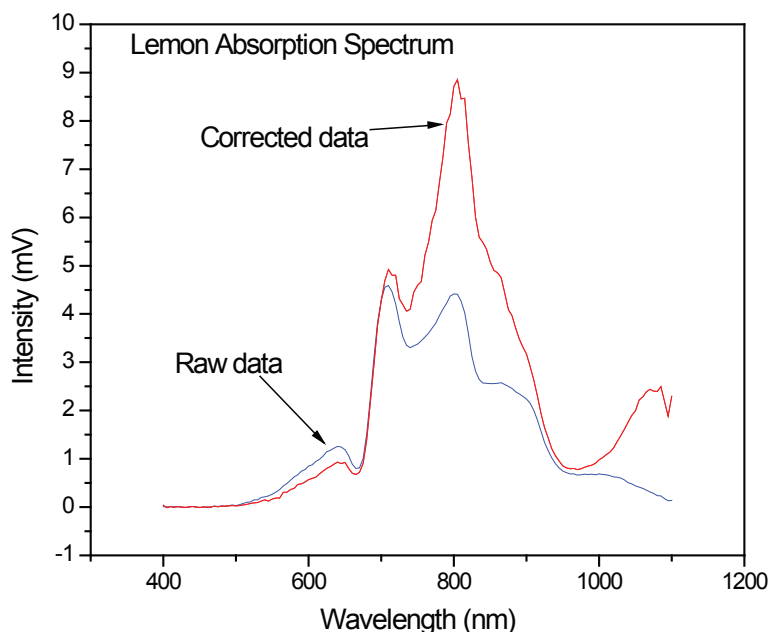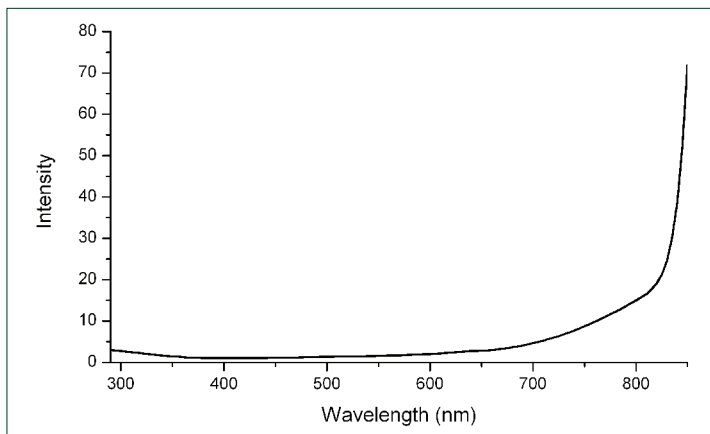

Figure 2. Typical "mcorrect" spectrum.

Building a Low-Cost Calibration Tool for Relative Response Corrections

A comparison was made between the spectrum obtained using the standard Model 1908 kit with a calibrated lamp and scattering block, and a flashlight with a tungsten bulb and a solid block of Teflon as a scattering block. The resulting data agreed within 3%, in the spectral range 290 – 850 nm. When a standard business card was used, the resulting data were significantly different, and a fluorescence signal was clearly evident around 420 nm. Thus, for relative spectral measurements, a flashlight with tungsten bulb and Teflon block can be used to calibrate the relative response function of a spectroscopic system.

> **NOTE:** A flashlight with a LED should not be used. Although a business card can be used in place of a Teflon block, the results are not quite as good.

Irradiance data from a calibrated lamp may be used with a tungsten bulb flashlight, following the same procedure described for an actual calibrated lamp, either from a file supplied by the lamp manufacturer, or read from a typical curve as shown in the Appendix.

Figure 3. Absorption spectrum of a lemon with raw data shown in blue and corrected data shown in red.
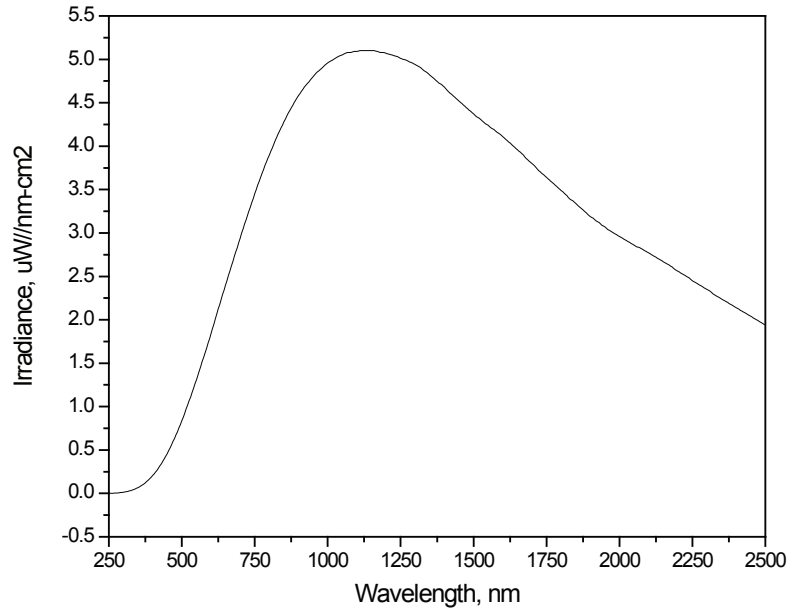
Appendix

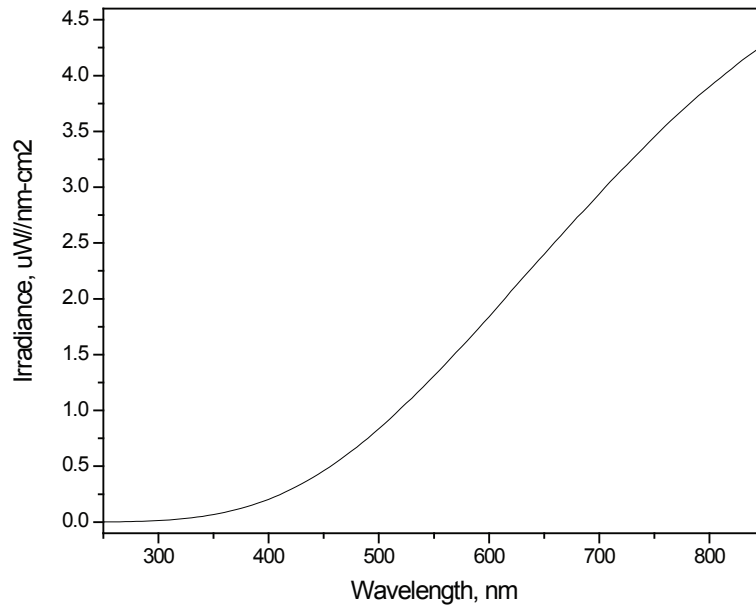Figure 4a. Full range of tungsten-halogen lamp spectrum.

Figure 4b. Zoom of 250 - 850 nm range of tungsten-halogen lamp spectrum.

References

1. Radiometric Corrections Tech Note S2, Spex Instruments, 11 March 1985.
2. Rutgers, G.A. "Absolute Spectroradiometric Measurements," NBS Special Publications 378, USGPO, Washington, DC, 1972.
3. Wyatt, C.L., "Radiometric Calibration Theory and Methods," Academic Press, New York, NY, 1978.