

Spectrophotometer Calibration

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Abstract

An overview of the working principle of a spectrophotometer is given. The instrument gives light intensity with respect to wavelength. A method to transform the acquisition variable to energy is shown. It is shown how to calibrate the acquisition variable with a low-pressure sodium and high-pressure mercury lamp. Finally, the acquisition variable is transformed into an equidistant sequence, and the spectrum intensity is scaled by the acquisition variable transformation.

1 Introduction

Miniature optical spectra-photometers controlled via USB offer practical means for simple optical and infrared experiments today. They use a linear CCD array, a grating and a cylindrical lens to disperse the light over the full length of the CCD array. The input to such spectra-photometers is generally a large-core multimode fiber with a lens at its input side. The CCD array are essential silicon detectors which nominally cover UV/VIS/IR range: 350 nm to 1100 nm wavelength range. Such spectra-photometers are also equipped with a calibration information which includes quantum efficiency versus wavelength variation as silicon detectors, used in the CCD, exhibit highly wavelength-dependent quantum efficiency. This calibration information allows the user to obtain a near flat intensity response. In addition to intensity calibration, there is a need for wavelength calibration which stems from the fact that in the linear CCD array, the detectors are equidistant in space, while the refraction of the optical beam shift on the grating is only approximately linearly dependent on the wavelength. Manufacturers of such spectra-photometers hence build in this wavelength calibration into the con-

trol software of the equipment. The reading of such spectra-photometers hence delivers a two-column array of wavelength $\lambda(k)$ and power spectral density $S_\lambda(k)$ where both the wavelength and the intensity are given in $n + 1$ points, where $n+1$ is the number of pixels in the linear CCD array and $0 \leq k \leq n$. Both values are corrected from the intrinsic reading. The subscript λ in S_λ means that the spectral density is given relative to wavelength. The purpose of this note is to describe wavelength calibration of a spectra-photometer.

2 Calibration procedure

Wavelength calibration is generally performed using reference gases. Gases are found in sodium and mercury vapor lamps. The principal atoms are sodium (Na) and mercury (Hg). When measured with a spectrophotometer, the wavelengths of the emission and absorption lines differ from expected values. The spectrophotometer is calibrated using a low-pressure sodium and a high-pressure mercury vapor lamp.

3 Working principle

The spectrophotometer measures the energy intensity of the observed light source with respect to wavelength. The light encounters a grating which diffracts the incoming photons depending on their frequency. Diffracted photons land on different pixels of the linear charge coupled device (CCD) sensor placed inside the instrument. When a photon lands on the pixel, depending on its frequency and energy, an electron results from the photovoltaic effect. The electrons fill the quantum well of the pixel. Measuring the number of electrons within a set exposure time yields a digital quantity called

counts.

The physical phenomena which is narrow spectral lines is ambiguously hidden. The true spectrum of the gas is composed of Lorentzian-shaped spectral lines. Observing the spectrum with a spectrophotometer distorts the shape and width of the spectral lines. If the spacing of the spectral lines is small enough compared to the resolution of the spectrophotometer, the comblike appearance will be distorted or even completely washed out.

The measurement system consists of a lens, connectors, cable, grating, silicon detector as well as an analog-to-digital converter. The observed light passes through a small lens fixed on the connector of a 200 μm optical cable. Following through the cable it reaches the second connector into the instrument. Each part of the system contributes to the total system transfer function. The resulting spectra is a convolution of the physical phenomena and the system transfer function. The desired data are representable as a function $L(\varepsilon)$ and the output of the measurement system is representable as

$$S(\varepsilon) = \int_{-\infty}^{\infty} T(\varepsilon - \tau) L(\tau) d\tau$$

where $T(\varepsilon)$ is the system transfer function.

Typically, a linear CCD array consists of three regions: the photosensitive region, transfer region and output circuit region [1].

The photosensitive region consists of MOS capacitors with an electrode attached on top of the silicon dioxide on the semiconductor substrate surface. When voltage is applied between the electrode and the substrate, a depletion layer is formed in the region near the interface of the silicon dioxide and semiconductor interface, causing this region to become a low-energy-level potential well for the minority carrier. If a signal charge generated by light radiation is injected into this potential well, these signals are temporarily stored as analog quantities [1].

The transfer region's scanning function transfers each signal charge generated in the photosensing region to the output circuit in turn. Multiple MOS capacitor units are arranged in close proximity and signal charge is transferred from one MOS capacitor to the next. Since two wells operate as a unit, one pixel in the photosensing region corresponds to two potential wells. The total transfer efficiency is

defined as the percentage of the charge transferred to the final well [1].

The output region has a function to convert the signal charge which is transferred from the transfer region into voltage. It consists of a floating capacitor. The voltage of the floating capacitor is varied according to the signal charge [1].

When the input light is zero, the output voltage is the dark signal. The dark signal in the photosensing region depends on the value of the *integration* time. The dark signal in the transfer region is proportional to the signal transit time of the CCD analog shift register area. Therefore, as the operating speed decreases and the ambient temperature rises, the dark signal increases and the dynamic range of the video signals decreases [1].

Before taking a measurement it is necessary to compensate the dark signal. Since the dark signal depends on the operating speed, a high integration time is set. The dark signal is then measured, averaged and further subtracted from the measurement.

4 Calibration

The spectrophotometer used (Photon Control SPM002-CH) has $n = 3648$ pixels in the spectral range between $\lambda_1 = 334.710$ nm to $\lambda_n = 1016.000$. All the wavelengths in between these two end values are denoted with λ_k , where $1 \leq k \leq n$ with the understanding that the wavelengths do not depend on k linearly. The average wavelength separation between the pixels is given by

$$\Delta\bar{\lambda} = \frac{\lambda_n - \lambda_1}{n - 1} = 0.1868 \text{ nm.} \quad (1)$$

The spectrophotometer gives light intensity with respect to wavelength. We are interested in the number of photons with certain energy. Therefore, the wavelengths (in nm) given by the spectrophotometer are transformed into energy:

$$\varepsilon = \frac{hc}{\lambda}, \quad (2)$$

where $k = 1, 2, \dots, 3647$, c is the velocity of light and h is Planck's constant.

The acquisition variable, which is now energy, is not calibrated. The emission lines of the measured lamps do not fit the spectral lines of the principal atoms. This can be seen in Table 1 which shows

Table 1: Spectral lines of sodium and mercury and measured emission lines of the high-pressure mercury (HPM) and low-pressure sodium (LPS) lamps. The unit is nanometers.

Hg	HPM	Na	LPS
365.015	365.620	588.995	589.570
404.656	405.300	589.592	590.130
435.833	436.580	818.326	818.680
546.074	546.630	819.482	819.800
576.960	577.420	-	-
579.066	579.480	-	-

emission lines, but in wavelength for clarity. The error is approximated with a straight line, as shown in Figure 1a. Energy is the x-axis and the y-axis represents the error in energy. Each point (cross) shows the difference in energy between the measured emission line and its table value. A straight line is computed such that, for all points, the vertical distance to the straight line is minimized.

The first step, to compute the straight line, is to calculate the difference in energy for the $m = 10$ data points:

$$\Delta\varepsilon_i = \varepsilon_{i,measured} - \varepsilon_{i,table} , \quad (3)$$

where $i = 1, 2, \dots, m$. In the following equations, $\varepsilon_{i,table}$ is written as ε_i for clarity. The second step is to find the coefficients α and β which describe the line:

$$\Delta\varepsilon_i = \alpha + \beta\varepsilon_i + e_i , \quad (4)$$

$$e_i = \Delta\varepsilon_i - \alpha - \beta\varepsilon_i . \quad (5)$$

The line has to minimize the sum of the mean-square values of the error parameter:

$$\frac{\partial}{\partial\alpha} \sum_i^m e_i^2 = \frac{\partial}{\partial\beta} \sum_i^m e_i^2 = 0 \quad (6)$$

$$\sum_i^m (2\alpha + 2\beta\varepsilon_i - 2\Delta\varepsilon_i) = 0 \quad (7)$$

$$\sum_i^m (2\beta\varepsilon_i^2 - 2\varepsilon_i\Delta\varepsilon_i + 2\alpha\varepsilon_i) = 0 \quad (8)$$

The y-intercept is given by:

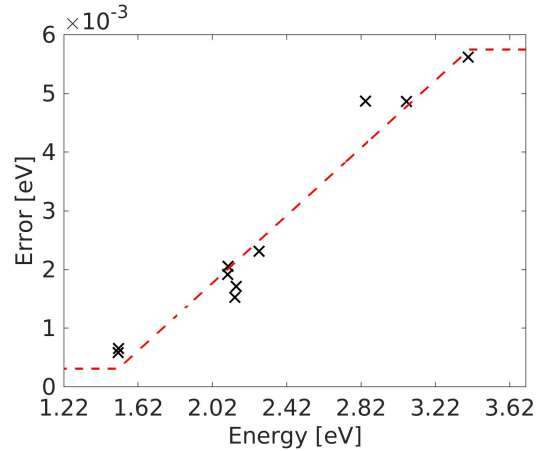
$$\alpha = \frac{1}{m} \sum_i^m \Delta\varepsilon_i - \frac{1}{m} \beta \sum_i^m \varepsilon_i \quad (9)$$

The slope of the line is:

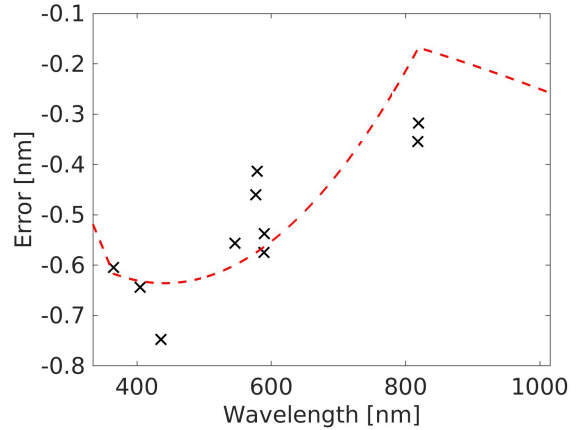
$$\beta = \frac{\sum_i^m \left(\varepsilon_i - \frac{1}{m} \sum_j^m \varepsilon_j \right) \left(\Delta\varepsilon_i - \frac{1}{m} \sum_j^m \Delta\varepsilon_j \right)}{\sum_i^m \left(\varepsilon_i - \frac{1}{m} \sum_j^m \varepsilon_j \right)^2} \quad (10)$$

The straight line is given as a sequence:

$$y[n] = \alpha + \beta \cdot \varepsilon[n] . \quad (11)$$



(a)



(b)

Figure 1: Difference between the measured emission lines (of the high-pressure mercury and low-pressure sodium lamps) and the emission lines of mercury and sodium, respectively. The error is approximated with a straight line. When transforming from energy to wavelength, the straight line is distorted.

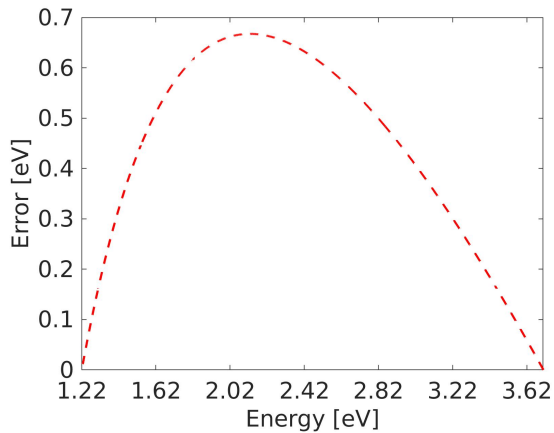


Figure 2: Calculated error given by subtraction of the energy acquisition variable and an ideal linear energy line.

The approximation is shown in Figure 1a. For clarity, by undoing the wavelength to energy transformation, the data $\Delta\varepsilon_i$ and straight line $y[n]$ are shown in Figure 1b.

Finally, the calibrated energy sequence is:

$$E[n] = \varepsilon[n] + y[n] . \quad (12)$$

We want to have equidistant points of energy. The acquisition variable energy, although now calibrated, is not linear. To show this, a line connecting the minimum and maximum value of the acquisition variable is computed:

$$t[n] = E[0] + \frac{E[3647] - E[0]}{3647} \cdot n, \quad (13)$$

where $n = 0, 1, \dots, 3647$. The calculated linear line $t[n]$ is subtracted with the values of the acquisition variable $E[n]$. The result is shown on Figure 2. To transform the calibrated energy sequence into an equidistant sequence, we use the Matlab function *resample* which TODO explain what it does.

The spectrum intensity when transforming from the wavelength to the energy acquisition variable, scales with the square of the wavelength. This is corrected by the following equation:

$$\frac{\partial S}{\partial E} = \lambda^2 \frac{q}{hc} \frac{\partial S}{\partial \lambda}, \quad (14)$$

where $q = 1.60217733e-19$ is elementary charge in J.

5 Conclusion

A spectrophotometer gives light intensity with respect to wavelength. The wavelength acquisition variable can be transformed to energy in order to yield the photon count. The acquisition variable can be calibrated using a low-pressure sodium and a high-pressure mercury calibration lamp. Furthermore, the dark signal, as well as the non-equidistant acquisition variable have to be corrected.

Acknowledgment

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References

- [1] "CCD linear image sensors", Toshiba: *Application Notes and Technical Articles*, 2001.
- [2] R. de la Fuente, "White Light Spectral Interferometry as a Spectrometer Calibration Tool", *Applied Spectroscopy*, vol. 68, no. 5 (2014).