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CCDS IN SPECTROSCOPY UTILIZATION OF STANDARDS

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June 1996

Reprinted from Laser & Optronics,
Elsevier Communications

Reprint Number: R14 | Cover Sheet Updated: Mar 2019 | OptronicLabs.com

CCDs in Spectroscopy

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CCDs were originally developed for aerospace and astronomical applications, but have been developed for commercial uses ranging from camcorders to fax machines. When coupled to spectrographs, their speed and sensitivity have transformed many analytical spectroscopic techniques. Raman, fluorescence, ICP, and many other spectroscopic techniques that were traditionally slow and difficult have gained from the use of CCDs. In some cases however, CCD systems have been substituted for scanning systems without full consideration of their equivalence.

CCD-based spectroscopic instruments are not necessarily equivalent to scanning systems.

This article will review some general guidelines in determining the suitability of CCD systems for any spectroscopic method. In particular, common sources of error will be analyzed to establish what, if any, differences exist between CCDs and established scanning systems. Also, although CCDs are referred to throughout the text, other multi-channel devices such as diode-arrays or CIDs are expected to behave similarly.

Analytical spectroscopic techniques can be, on a simplistic level, categorized as relative or comparative. Relative techniques are those where a particular spectral distribution, often associated with a particular chemical species, varies in intensity according to the concentration of that species. Such techniques include Raman, fluorescence, phosphorescence, and ICP. Comparative techniques are those where one spectral distribution is used in the calibration of the instrument, and another is present during analysis. Examples of these latter techniques include transmission, reflection, and spectroradiometry. It is this distinction of whether the calibration spectrum is the same as, or different from, the test spectrum that dictates the magnitude of the errors for CCD systems. The spectra of common light sources — sunlight, LEDs, arc lamps, incandescent lamps, fluorescent lamps, and lasers — are so varied that spectroradiometric measurements probably represent the most stringent test of CCD systems. The rest of this article will therefore concentrate on differences between scanning and CCD systems in spectroradiometry, though analogies to other measurements should be implied.

In December 1995, the Council for Optical Radiation Measurements (CORM) stated, "While it is possible to produce meaningful spectroradiometric measurements from multi-channel instruments, the practical difficulties are generally ignored in system implementation and treatment of data leading to incorrect or misleading results."[1] This statement reflects the fact that many suppliers market CCD systems for applications they know little about, and most software packages manipulate data as though it were obtained from a scanning system.

To highlight some of these difficulties, the following discussion will deal with four specific types of errors:

1. Fundamental errors, common to all CCD systems;
2. Inherent errors, common to all CCD systems:
3. Errors associated with practical designs, common to most CCD systems; and
4. Unusual errors, found in some CCD systems.

Fundamental Errors

Any practical system would be expected to give errors, but an important question for any technique is: If the instrument behaved ideally, would it give the correct result? This question can be answered since CCD spectrograph systems can be easily modeled for any given input spectrum using diffraction theory[2] and simple geometry. To test the performance of our "ideal" system, we should assess the errors for narrow, medium, and wide spectral shapes using a typical high-quality configuration currently marketed. The configuration chosen is: a 200-mm-focal-length spectrograph with a 133-g/mm grating and 0.2 mm entrance slit; a CCD with 512 pixels of 25 μm width along the wavelength axis direction, binned vertically over the entire height of the image, a spectrograph include-angle ($\alpha_c + \beta_c$) of 18 degrees and the CCD plane inclined to the optical axis (γ) at 11 degrees; all components except the CCD are 100% efficient, and the CCD has a typical silicon spectral responsivity. This a typical configuration chosen for visible measurements, which probably represents the greatest use of CCD systems in spectroradiometry.

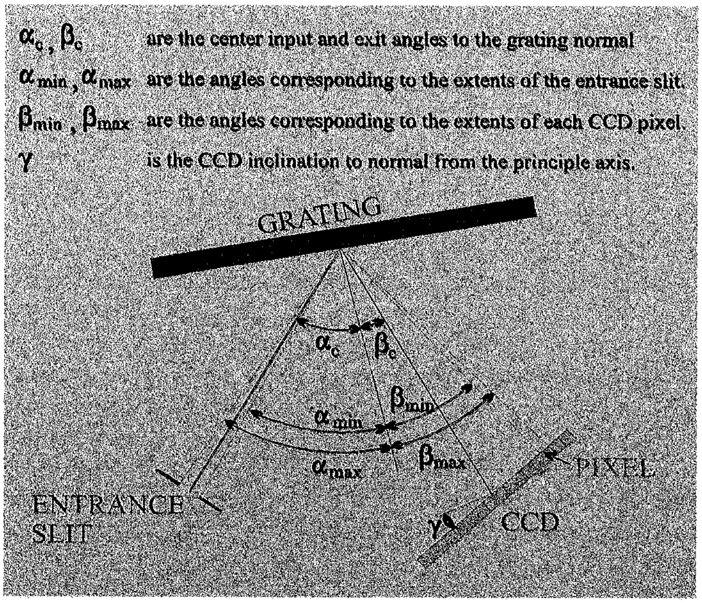
α_c, β_c are the center input and exit angles to the grating normal
$\alpha_{min}, \alpha_{max}$ are the angles corresponding to the extents of the entrance slit.
β_{min}, β_{max} are the angles corresponding to the extents of each CCD pixel.
γ is the CCD inclination to normal from the principle axis.

Figure 1. A basic arrangement of a CCD spectrograph with definitions of terms. Actual spectrographs will differ from this, generally incorporating urved mirrors or gratings.

Figure 1 shows the basic arrangement of the CCD spectrograph, with definitions of terms used in the calculations. The signal at each pixel is given by:

$$s = \int_{\alpha_{min}}^{\alpha_{max}} \int_{\beta_{min}}^{\beta_{max}} R(\lambda) \times \Phi(\lambda) \times d\beta \times d\alpha \qquad (1)$$

where

$$\lambda = \frac{10^6 (\sin\alpha + \sin\beta)}{n}$$

λ is the wavelength [nm], n is the grating density [g/mm], $R(\lambda)$ is the responsivity of silicon [A/W], and $\Phi(\lambda)$ is the input spectral flux [W].

In scanning spectroradiometry, the system is calibrated with a suitable source of known values at each wavelength. The current approach to CCD radiometry is the same, taking the center of each pixel to establish the respective wavelengths. In this example, we take the values for a blackbody source at 2856 K, though this method works equally for FEL or similar NIST standards. The known values of the standard for the center wavelengths of each pixel is then divided by the signal calculated for the respective pixels to give the instrument response $\Gamma(\lambda)$.

$$\Gamma(\lambda) = \frac{\Phi^s(\lambda)}{s^s(\lambda)} \qquad (2)$$

The spectral distribution of a test source $\Phi^t(\lambda)$ can now be calculated from observed signals $s^t(\lambda)$ at each pixel by:

$$\Phi^t(\lambda) = s^t(\lambda) \times \Gamma(\lambda) \qquad (3)$$

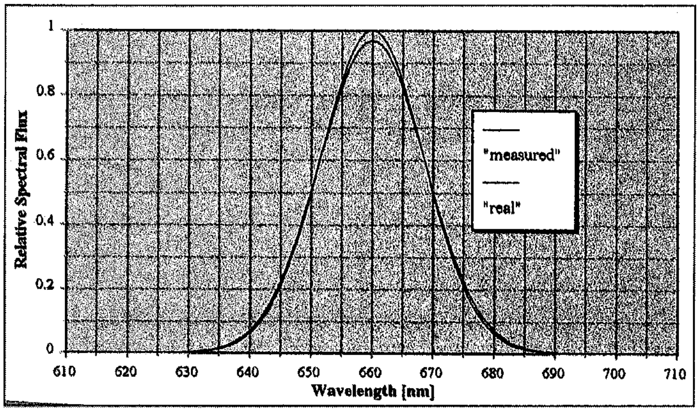

Figure 2. A Gaussian ("real") and the theoretical ("measured") spectral distributions for the ideal spectrograph described in the text.

However, the signals $s^t(\lambda)$ at each pixel can also be calculated from Equation (1), so the errors inherent in the calibration/measurement process can be determined. Figure 2 shows the measured values that would be obtained for a Gaussian spectral distribution of 20 nm full width at half maximum (FWHM). Although a theoretical test spectrum is used, it is fairly typical of red LEDs that may be encountered commercially.

The integrals under each curve are in very close agreement, but significant differences are seen between the "real" and "measured" spectral distributions. Table 1 summarizes the "measured" errors in peak spectral flux value, FWHM, luminance, and chromaticity values.

As can be seen from Table 1, the properties dependent on the absolute spectral values such as peak spectral flux, FWHM, and luminance show fairly large errors. Values that are relative measures, such as the x, y, and z chromaticities, show negligible errors. As the FWHM of the test spectral distribution becomes narrower, all of these errors rapidly increase; whereas wider FWHM values show decreases, becoming zero for a continuous spectrum resembling the calibration source. In contrast, a similar treatment for a typical scanning system with 0.2-mm slits gives negligible errors except for sources with very narrow spectral distributions such as lasers. The reason for this difference is that in applying the techniques of scanning spectroradiometry to CCD systems, the actual distribution of light and interdependence of pixels in representing a particular wavelength is ignored.

Although the fundamental errors associated with the typical CCD system outlined are quite large, considering they represent the best possible situation, they are generally dwarfed by the inherent errors found in commercially available systems.

Inherent Errors

The basic assumption in the simplistic approach to spectroradiometry usually adopted in CCD systems is: Each

Table 1.

Property	Real	Measured	% Error
Peak Spectral Flux	1	0.968	-3.2
FWHM	20	21.2	6.0
Luminance (lm)	948.5	954.5	0.6
x	0.7279	0.7280	0.01
y	0.2721	0.2720	-0.004
z	0.0000	0.0000	0.0

Properties of the "real" and "measured" spectral distributions shown in Figure 2.

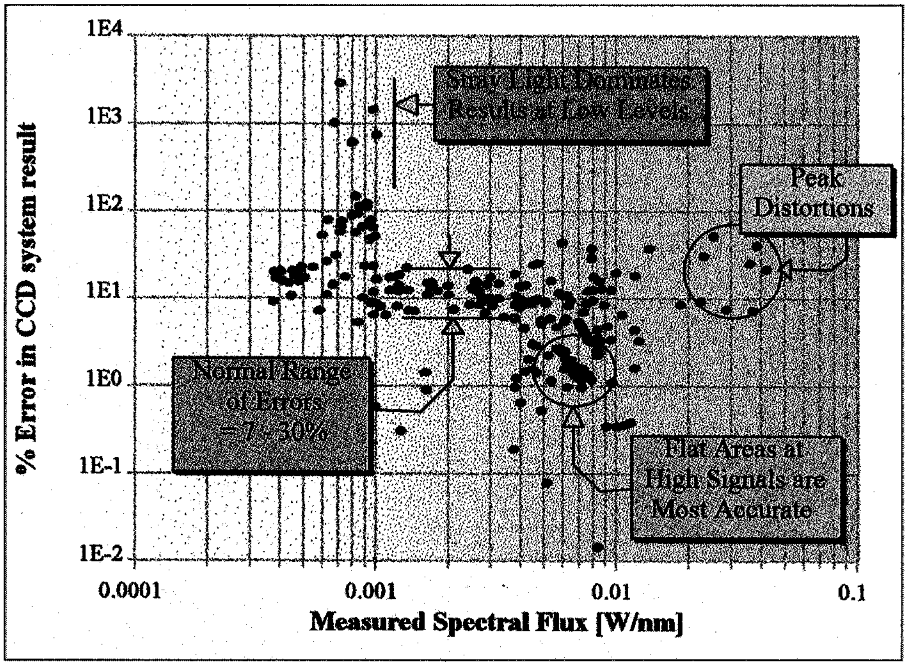

Figure 3. An Error/Intensity diagram, illustrating the sources of errors occurring in the measurement of fluorescent lamps with even the best CCD systems.

pixel corresponds to a narrow range of wavelengths dictated by diffraction; any mechanism that places other wavelengths at that pixel will produce an error. We have already established from Equation (1) that the entrance slit affects the distribution of wavelengths on each pixel. The lack of consideration of this fact is the basic reason for the existence of fundamental errors in the method. Other mechanisms, associated with non-ideal behavior, generally produce far greater errors. These are usually referred to as stray light errors, but may be divided into near-field (within three or four pixels from the correct position) and far-field (affecting all the pixels, but not necessarily equally). They are expressed as a ratio of the effective stray light at a pixel to the total effective flux within the spectrometer.

Single spectrometers used in scanning systems normally exhibit far-field stray light levels of about 10^{-3} to 10^{-4} in the ultraviolet. However, the spectrographs employed in CCD systems show much higher stray light levels since the CCD can "see" all of the inside rather the just the active optics. In practice, this means that CCD systems are limited to a one- or two-decade dynamic range in the UV, except for monochromatic sources. In the visible and infrared ranges, this problem is somewhat lessened, but generally three decades of dynamic range is only achievable on the best (and largest) systems. Size is important in considering suitability since, as a very general "rule of thumb," far-field stray light decreases with the square of the spectrograph focal length. Apart from limiting dynamic range, stray light can often overwhelm any real signal that exists at the correct wavelengths. In the UV, it is not unusual to record intensities four decades higher than the true spectrum of the source. Even in the visible, care must be taken for narrow spectral sources, such as the LED example in the previous section, to prevent luminance and chromaticity values being dominated by stray light errors.

Apart from limiting dynamic range, stray light can often overwhelm any real signal that exists at the correct wavelengths.

Wavelength accuracy is a fundamental requirement of spectroradiometry, since the calibration standard intensity values are a function of wavelength. The wavelength accuracy is normally determined by scanning a narrow spectral line in fine increments to determine the peak position. However, without a detailed knowledge of the instrument slit function, the residual error in the determination must be the scan interval. This also applies to a CCD system, except the scan interval is one pixel. For a CCD system therefore, these relatively high wavelength errors will produce correspondingly high errors in results.

Errors Associated With Practical Designs

The above section discussed far-field stray light in general terms. For two spectrographs of the same focal length, the magnitude of this problem can often reflect the quality of optics and attention to detail in the design. Near-field stray light generally comes from aberrations such as astigmatism and coma, and from imperfections in the optics and grating. Thus, although not necessarily true in all cases, a low far-field stray light level is often associated with low near-field stray light.

Another form of stray light, almost unique to CCD systems, is "correlated" stray light. Often a CCD will be placed behind a window, especially if it is cooled. Reflections from the CCD surface will therefore hit this window and be reflected back — but not to the same pixel. A "ghost" spectrum will therefore be superimposed on the original, but since the incident angle is not constant, the wavelength shift also varies. The severity of this problem and the shifts involved generally depend on the exact design of the spectrograph and CCD.

Sharp variations in the responsivity of the system can produce localized distortions and errors. For instance, unlike the smooth, but low-resolution CCD response curves supplied by many manufacturers, some (if not all) CCDs exhibit large changes in their response over small wavelength intervals. If this type of response were applied to the fundamental error calculations, much larger errors in the spectral distribution would have resulted.

Most CCD systems have a very limited dynamic range, and rely on changes in integration time to accommodate high and low intensities. Many of the "top of the range" (and some cheaper) CCD systems use a mechanical shutter to expose the pixels for the required integration time. At short integration times, variations in the speed of the shutter can be a large source of error in measurements. Also, many shutter designs result in some pixels of the CCD being exposed longer than others, with unpredictable effects.

Since CCD systems are often required to cover wide wavelength ranges, multiple-order diffraction components need to be eliminated. Some companies mount blocking filter components directly onto the CCD which, provided there are no edge effects, is a good solution. Others apply a somewhat dubious elimination by calculation, sometimes with limited success.[3] Many suppliers are either unaware of, or choose to ignore, the problem, though it is difficult to see any justification to this approach.

To illustrate that significant errors are found even in the best CCD systems, Figure 3 shows the errors found for a fluorescent lamp measurement with a top-of-the-range instrument. The percentage error is plotted against measured spectral flux since this shows a distinct pattern, with particular regions indicating the types of errors described above.

Unusual Errors

The prior discussion assumes that the manufacturer of the CCD system has produced the bias, amplification, and digitization electronics to the highest standard. Occasionally however, a system is found to not respond linearly with light intensity.[4] It should be obvious that any such system is totally unsuitable for spectroradiometry.

Sometimes software programmers introduce "features" that are inappropriate to spectroradiometry, such as creating an equal-increment file by linearly interpolating pixel signals. This linearization, as it is called, may be valid for broad, slowly changing spectral data. However, it will inevitably distort any narrow spectral features since it assumes the data is a smooth, finely sampled, continuous function rather than the coarsely sampled histogram it really is. Some manufacturers take this practice to extremes and actually end up with more data points than they had original pixels.

> Other mechanisms, associated with non-ideal behavior, generally produce far greater errors.

Conclusion

The fact that users may obtain reproducible results using CCD systems may give the erroneous impression that those results are accurate. There are fundamental and practical errors associated with treating each pixel as representing a particular wavelength since, as discussed, each wavelength is normally detected by several pixels. Although stray light and other errors are inherent, some errors are introduced by the method and treating the CCD system as though it is a scanning system.

For relative spectroscopic techniques, CCD systems provide a useful enhancement since all pixel signals, including those due to stray light, increase linearly with intensity provided the spectrum remains constant. For comparative techniques, though, many applications may not be suited to their use with current methods. Given this situation, CORM's recommendation for future "additional research on the use of multi-channel instruments used for spectroradiometric measurements" seems a good one.

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