

Feature Article

The Role of Detectors in Spectroscopy

Salvatore H. Atzeni, Linda M. Casson

The role of the detector in optical spectroscopy has evolved over the years, as advances in technology, driven by application requirements, have made the detector much more than simply a transducer at the end of an optical arrangement. Earlier instruments generally consisted of a relatively high-cost spectrometer and a low-cost detector such as a photomultiplier tube (PMT). Thus, the detector was an accessory to the spectrometer. As detector technologies improved, the capability, complexity and expense of the detector increased, placing a lower emphasis on the capabilities of the spectrometer, whose design and capabilities remained relatively constant during the same time period. Today, many researchers accept the notion that the detector is the heart of a spectroscopic system, and the optical subsystem is more of an accessory to the detector. The evolving role of the detector, from an accessory to a key component, was driven by rapid advances in technology as well as cost reduction of complex technologies. In many cases, modern spectroscopic instruments are designed as an integrated system in which the detector is an integral part of the spectrometer or spectrograph, making it possible to optimize the spectroscopic system performance at even lower cost. In this Article, we discuss some common detector choices, their roles in the spectroscopic detection arena, and salient points related to selection, advantages and key performance metrics. Examples of HORIBA Jobin Yvon, Inc. detector products and technologies are provided to illustrate sample implementations that address common application requirements.

Introduction

Optical methods play an increasingly important role in the modern world. From the telecom industry to the food industry, light measurement instruments make a large contribution to the way we live. Optical spectroscopy allows measurement of various phenomena, often in a safe, nondestructive manner, with possibilities for remote sensing when a sample is located far from the instrument. Many techniques allow excellent quantitative analysis, with selectivity and sensitivity towards specific analytes. All optical spectroscopic measurement systems include a detector, but depending on the application, may also include a light source to stimulate the sample being measured, and a filter or dispersive element (commonly a diffraction grating or prism) which separates the light into its constituent colors before being measured by the detector subsystem.

Optical detectors used in spectroscopic instruments are often classified as either single-channel detectors (SCDs) or multichannel detectors (MCDs). Single-channel detectors have one active sensing element that acts as single transducer. Photons reaching the detector, within its operating wavelength range, are absorbed by the active material of the detector and encoded as an electrical signal. The output signals produced by the detector vary according to the detector specifications, but generally include analog (voltage or current) and digital (pulse-counting) domains. A spectrometer with its PMT is operated by moving the diffraction grating to present different wavelengths to a focal point at the exit slit, where the PMT will sequentially record the signal, one wavelength at a time. In contrast, multichannel detectors have multiple active sensing areas which collect many wavelengths simultaneously at the focal plane of a spectrograph. No exit slit is used in this arrangement. Each arrangement has advantages and disadvantages, and

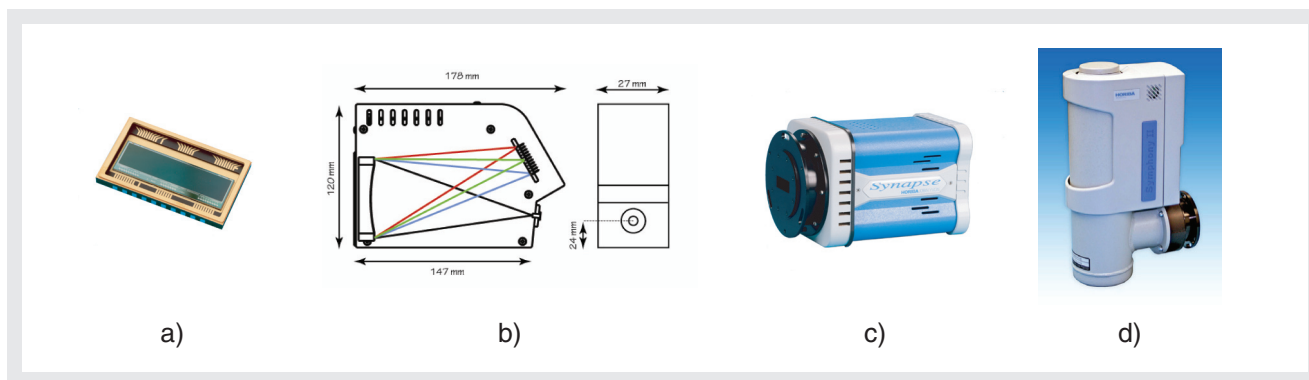


Figure 1 From left to right: a) A typical CCD sensor chip [e2v Technologies, Ltd. Model CCD30]; b) shown mounted in an integrated spectrograph [HORIBA Jobin Yvon, Inc model VS-140]; c) mounted in a thermoelectrically-cooled housing [HORIBA Jobin Yvon Inc. model SYNAPSE]; d) mounted in a cryogenically-cooled Dewar [HORIBA Jobin Yvon, Inc. model SYMPHONY-II].

it is the application requirement that defines which configuration is most suitable.

While they are excellent photon transducers, optical detectors exhibit some intrinsic background, even when no optical signal is present. Most detectors used for spectroscopy benefit from cooling to reduce this background signal. As the detector is cooled below room temperature, often to very low operating temperatures, the background signal and its associated noise component is reduced. Common cooling techniques involve thermoelectric as well as cryogenic cooling using liquid nitrogen. To eliminate condensation and the potential for corrosion, the sensors themselves are often mounted in a vacuum housing and sealed using hermetic methods, ensuring years of maintenance-free use.

In this Article, we offer an overview of many commonly used detectors for spectroscopic applications, from the UV (150 nm) to the mid-IR (20 microns). As many devices exist in the marketplace, we choose to limit the scope of this discussion to scientific-grade detectors,

which differ considerably from consumer-grade products in terms of performance, complexity and cost.

Single-Channel Detectors (SCD)

Probably the best known detector is still the classic PMT, which offers good performance in detecting photons across a relatively wide wavelength range at modest cost. However, many types of single-channel detectors are available on the market today. They are classified according to the method of optical to electrical conversion. First, a photon is absorbed by the material creating an electron-hole pair. If the generated photoelectron is further emitted from the material, becoming available for collection or multiplication, the device is called a photoemissive device, or one based on the external photoelectric effect. PMTs are the most common example of this type of detector. If instead no emission takes place but the photogenerated electron-hole pair is available for the current circulation in an external circuit, we call this an internal photoelectric device. Solid state detectors fall in this category, but may be subdivided

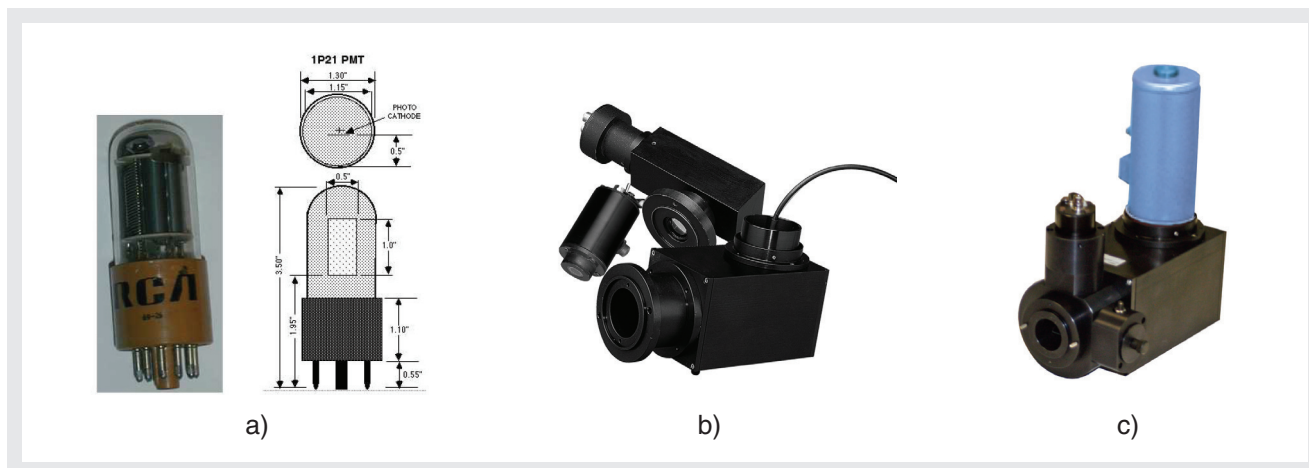


Figure 2 Examples of common SCDs. From left to right: a) a standard, side-on PMT; b) a thermoelectrically-cooled InGaAs detector and optical housing; c) a cryogenically-cooled InGaAs (HORIBA Jobin Yvon model DSS-IGA-020L with 1427C housing). The optical coupling from the exit slit to the small active area of the detector is accomplished using an elliptical mirror, compressing the slit height by 6:1.

Feature Article

The Role of Detectors in Spectroscopy

into photovoltaic (photodiodes, for the visible-NIR range) and photoconductive (or photoresistive, for the MIR). Although photoemissive devices frequently have gain, providing higher sensitivity, they have the drawbacks of vacuum tube technology, requirement for high-bias voltage and limited spectral range of operation.

A third category of photodetectors is thermal detectors. These operate according to a two-step process: first, radiation is dissipated in an absorbing material; then the resulting small increase in temperature is measured by a change in the electrical properties (such as resistance) of the material. Although these detectors often cover a broad spectral range (visible - MIR), they have much lower sensitivity compared to the other categories of photodetectors and are not often used in spectroscopy except in limited cases in MIR systems. Table 1 summarizes typical characteristics of these devices.

Table 1 Categories of single-channel detectors

| Category | Detector | Typical active area | Spectral Ranges |
|--|---------------------------|--------------------------------|------------------------------|
| Photoemissive (external photoelectric) devices | Photomultiplier tube | Few mm up to 25 mm diameter | < 100 nm - 1650 nm |
| | Semiconductor photodiode | 1 - 3 mm diameter | |
| Internal photoelectric devices | Avalanche photodiode | 20 - 80 μm diameter | 200 nm - 20 μm |
| | Photoconductive detector | 1 - 2 mm diameter | |
| Thermal detector | Thermocouple (thermopile) | 10 - 20 mm diameter | |
| | Bolometer (or thermistor) | 1 - 2 mm diameter | 300 nm - > 100 μm |
| | Pyroelectric | 1 - 2 mm diameter | |

Detectors are selected based on experimental requirements. The first selection criterion is the wavelength range to be measured. In many cases this will narrow the choice down to one or two detectors. For example, if the wavelength range is 7 - 15 μm , an HgCdTe detector will be the only option. However, if the wavelength range is 400 - 700 nm, there are several options with the choice of optimum detector depending on other experimental requirements. For steady-state measurements with high light levels and a sample that is not easily damaged by exposure to light, either an uncooled PMT; or uncooled or TE cooled silicon photodiode (especially if future research plans involve NIR measurements) would be a good choice. For extremely low light levels, a PMT with photon counting will be the best choice.

Table 2 shows the spectral response for the most commonly used solid state detectors. These detectors are

most commonly used for steady-state measurements, but in certain cases, when coupled to a fast amplifier, may also be used for time-resolved measurements. When two detectors cover a similar wavelength range, such as InGaAs and Ge, the choice is based on gain, noise factors and response at a specific wavelength of interest. Ease of operation, based on not needing liquid nitrogen may also be a factor.

Table 2 Typical Wavelength Ranges for HORIBA Jobin Yvon Solid State Detectors

| Solid State Detector | Wavelength Range | Photovoltaic (PV) or Photoconductive (PC) |
|--|--|---|
| Silicon | 200 - 1100 nm | PV |
| InGaAs | 800 - 1700 nm | PV |
| InGaAs (LN ₂) | 800 - 1550 nm | PV |
| InGaAs (2.2 μm , LN ₂) | 1.1 - 2.2 μm | PV |
| Ge | 800 - 1800 nm | PV |
| Ge (LN ₂) | 800 - 1550 nm | PV |
| PbS | 1 - 2.8 μm | PC |
| PbSe | 1 - 4.5 μm | PC |
| InSb | 2 - 5.5 μm | PC |
| HgCdTe (MCT) (others ranges available, depending on elemental composition) | 2 - 14 μm 2 - 20 μm | PC |

The next consideration is whether the measurements require temporal analysis. For example, fluorescence lifetime measurements provide a much more detailed observation of the molecular processes that occur in biology and biophysics, materials science, and chemistry than do steady-state measurements. The fluorescence lifetime τ of these materials generally ranges from a few picoseconds to hundreds of nanoseconds. Figure 3 shows an example of a fluorescence lifetime measurement on

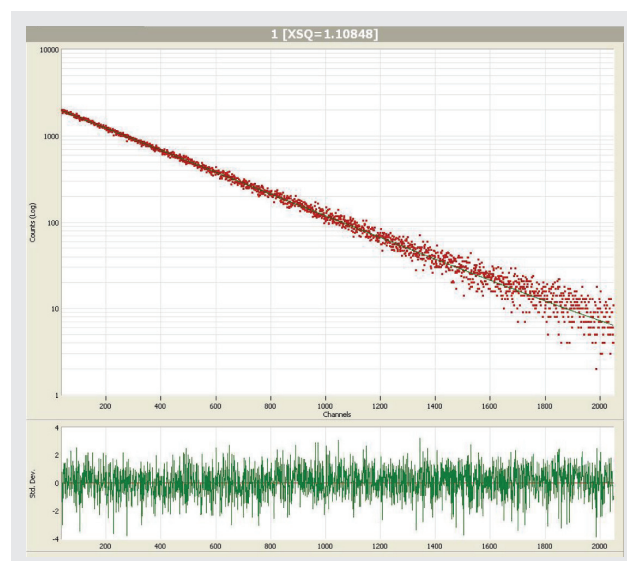


Figure 3 TCSPC measurement of KCl:Eu²⁺ exhibiting a lifetime of 1.19 microseconds.

KCl:Eu²⁺, obtained using Time Correlated Single Photon Counting (TCSPC).

There are 2 basic techniques for measuring fluorescence lifetimes: frequency domain measurements (such as in our MF² instrument) and time-domain measurements (including TCSPC and transient decay methods). By careful design of the electronics, a relatively inexpensive PMT can be optimized to perform picosecond lifetime measurements. With a carefully tuned fast amplifier-discriminator circuit, these PMTs can be used for TCSPC measurements to obtain lifetimes of biological, nanomaterials and other samples. The most popular models use a multi-alkali photocathode and cover the spectral range 185 - 850 nm, with some optimized for a particular subsection of this range. Other PMTs with different photocathode composition are optimized to extend the spectral response up to 1 micron. Variants that extend beyond 1 micron are available, however, these are costly and require careful handling as they can be easily damaged by excess light, rendering them less effective in the red and possibly destroying the tube. Generally, due to cooling requirements imposed by the higher thermionic emission, these models extend the usable range to approximately 1.6 microns. Photoluminescence (PL) and Electroluminescence (EL) lifetimes may be measured using the same experimental methods.

Another single-channel detector used in spectroscopy is the avalanche photodiode (APD)^[1]. This is a small device made of silicon or InGaAs, which may be operated in single photon-counting mode (Geiger Mode), sometimes abbreviated “SPAD”, which has very high gain and can be used to measure very low light levels. The disadvantage of this device is that it has very high dark current and associated shot noise, even for a detector with a diameter 80 microns or less, and must be cooled. Another new type of single-channel detector with potential use in spectroscopy is the discrete amplification photon detector (DAPD), which uses a novel approach to reduce the excess noise factor inherent in Geiger-mode APDs from approximately 1.3 to less than 1.05 with gain of 10⁵ with nanosecond risetimes. These devices may be produced from silicon or indium-gallium arsenide materials, offering a potential alternative to the PMT.

Multichannel Detectors

The most popular multichannel detectors for spectroscopy are silicon based charge-coupled devices (CCDs) with several thousand elements, or pixels, arranged in a rectangle. Inexpensive linear CCDs (and photodiode arrays) are available on the market, but in most scientific

applications, 2D CCDs are used. Scientific-grade CCDs exhibit high responsivity from the near-ultraviolet to the near-infrared (NIR) region of the spectrum — 200 nanometers to 1.1 microns. At longer wavelengths, the photon energy is lower than the silicon bandgap and the silicon becomes transparent to the incident photons. However, III-V semiconductor materials such as indium gallium arsenide (InGaAs) have a lower energy bandgap and can absorb the NIR photons (see Figure 4). For this reason, InGaAs arrays are the array detector of choice between 0.9 and 1.7 μm , and are now available up to 2 μm . Other multichannel detectors such as HgCdTe and InSb MIR arrays are available, but are not used as frequently, mainly due to their high cost.

In spectroscopy mode, a CCD works by first summing the electrical charges of the selected pixels in a column at the bottom of that column of the array into a “super-pixel”. This charge-shifting is called a parallel shift. The combined charge from each of these superpixels is transferred serially by the readout register to the output node amplifier. Here, these individual charges are read out and transferred to the ADC (analog-to-digital converter) and processed by the electronics. In a full frame (FF) CCD, the entire array is exposed to light. In a frame transfer (FT) CCD, the top half of the array is exposed to light and the bottom half is used to store the electrical charges before readout. This format allows faster spectral acquisition rate, and may sometimes be used for kinetics measurements. At the time of this publication, all CCDs supplied by the Optical Spectroscopy Division of HORIBA Jobin Yvon, Inc. are FF devices.

Silicon CCDs are available with various options to optimize performance. A basic, front-illuminated CCD may be coated with a phosphor to enhance its UV response. The phosphor absorbs the UV photons and re-emits green photons in the spectral range where the CCD is most sensitive. Modifications also can be made to the gate structure in order to improve the detection and raise the effective QE. This variation is called an “Open Electrode” (or “Open Poly”) CCD. In such a device, approximately one third of the gate is removed in the center of the pixel, allowing more light to reach the silicon, which improves detection. In a back-thinned CCD, the entire device is thinned so that it can be illuminated from the rear of the CCD which eliminates the problem of absorption from the polysilicon gates on the front. Because of the reduced silicon thickness, however, constructive and destructive interference may occur, resulting in an etalon effect that produces a pattern on the signal sensitivity, which can be difficult to correct

Feature Article The Role of Detectors in Spectroscopy

mathematically.

In another modification, CCD devices are made from special high resistivity material, creating deeper depletion layers in the silicon, resulting in a thicker active layer in which long-wavelength photons are more likely to be absorbed, enhancing the QE in the red region of the spectrum^[2,3].

Because CCDs are used for many applications, new types are appearing all the time. Pixel sizes are decreasing, which can improve spectral resolution, but at the same time decrease apparent sensitivity and dynamic range, since the charge capacity of each pixel decreases with size. Higher pixel densities also require longer readout times after exposure. Manufacturers of analytical spectroscopic instruments are constantly making tradeoffs in order to supply high sensitivity and speed while maintaining affordability.

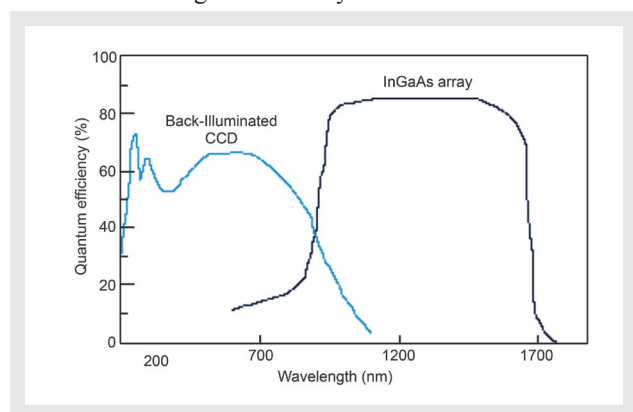


Figure 4 The spectral response of typical silicon and indium gallium arsenide (InGaAs) detectors shows the usefulness of InGaAs for near-infrared measurements.^[4]

Other types of CCD detectors are available that augment the capabilities of standard detectors by adding gain and temporal resolution/gating. These include the Electron Multiplying CCD (EMCCD) and the Intensified CCD (ICCD) detectors.

Electron-multiplier charge-coupled devices (EMCCDs)

An EMCCD may be thought of as a standard CCD with optional gain. They are often used for low-light applications with fragile samples, including biological applications and single-molecule work, where the option of integrating the signal for longer periods of time does not exist due to the transient nature of the sample.

EMCCDs are often used for imaging applications, and are commonly available in square formats intended to be used in microscopy, but are also available in other aspect ratios, making them more useful for spectroscopy. EMCCDs have on-chip gain, which is derived from a cascade register arranged between the serial register and a second output node. As the charge from each pixel is clocked out, the magnitude of this charge is increased as it steps through the gain register. Typically, the gain can be adjusted over a range of values, reaching as high as 103. While useful, there are some caveats in using this gain mode for quantitative work, and to alleviate this concern, many EMCCD sensors have both a 'standard' as well as a 'multiplier' output, giving the researcher the option of using the most appropriate mode for their particular experiment.

Intensified charge-coupled devices (ICCDs)

ICCDs also provide for amplification of the optical signal, here by passing it through an image intensifier tube (IIT). The IIT uses a standard photocathode material to convert incident photons to photoelectrons, much as a PMT does. These photoelectrons are then accelerated towards one or more microchannel plates (MCPs) which perform amplification in a manner analogous to the dynodes of a conventional PMT. The gain can be controlled by adjusting the bias voltage(s). The photoelectrons, now increased by several orders of magnitude, then strike a phosphor plate, which emits luminescence in the blue to green region of the spectrum. This light (often seen in videos as night-vision images) illuminates a CCD sensor which is operated in the integrating mode and read out in the normal manner. An ICCD has an image intensifier coupled to the CCD either by relay lenses, or more commonly, directly coupled using a fiber optic faceplate^[5]. An additional capability of the ICCD is its potential for time-resolved spectroscopy, as the IIT may be gated from DC (steady-state) to the nano- to picosecond time scale. This characteristic is useful for monitoring chemical kinetics or other time-resolved measurements including fluorescence and Raman. In the case of Raman time-resolved measurements, the ICCD is gated in a manner to pass the prompt Raman signal, but then block the longer lived fluorescence emission that may also be present in the sample. A common spectral imaging application involving a spectrometer coupled to an ICCD would be the temporal characterization of plasma emission.

Additional technologies

Other silicon-based multichannel detectors are now on the market. Most of these are read out by each individual pixel (rather than by shifting charge to the readout register as with a CCD), and the spectrum is reconstructed by the host software during post-processing. Some CMOS array detectors may be read nondestructively, so it becomes possible to use various integration times for each pixel without having to read out the entire sensor. This may be exploited to increase the dynamic range of a measurement. The scientific CMOS detector (sCMOS), a relatively new technology, is used for imaging — including machine vision such as inspection of defects in semiconductors, and is beginning to be used in microscopy. Infrared multichannel detectors, often called “focal plane arrays” are available in InGaAs, InSb and HgCdTe materials.

One interesting application using a 2D multichannel detector is called multi-track spectroscopy. In this type of measurement, a linear bundle of fibers is presented at the spectrometer entrance, with each of the fibers collecting light from a different analyte or part of an extended sample. The multichannel detector is divided into a number of horizontal strips, corresponding to the output from each fiber. In this manner, multiple spectra can be measured simultaneously.

Readout Electronics

In addition to the detector sensors themselves, the readout electronics associated with a detector, in particular with a multichannel detector, contribute to performance of the detector and spectroscopy system as a whole. HORIBA Jobin Yvon is well known in the industry for its superior readout electronics, especially for the Synapse CCD and InGaAs detectors. The use of correlated double sampling and other techniques produce detection systems with extremely low noise and high data fidelity allowing better overall performance of HORIBA Jobin Yvon spectroscopy systems compared to systems from other manufacturers using similar sensors.

Choosing a Detector

A multitude of detector options have been presented in this article. Here is a general set of questions to serve as guidelines to help the user narrow down the range of choices and select the most appropriate detector for the application.

1. What is the wavelength range of the measurement?
2. What spectral resolution is required for the

- measurement?
3. Can the application be addressed with a lower cost single channel detector or is a multichannel detector required?
4. Is the measurement steady-state (DC/continuous) or a time-resolved/kinetics measurement?
5. What is the expected light level or photon flux to be measured?
6. Are measurements being made on a fragile sample: one which is short-lived or susceptible to damage from exposure to light or other environmental factors?
7. What is the size/form factor of the light focused on the spectrometer entrance slit to be analyzed (such as spot or vertical line)?
8. Will the choice of this detector allow the user to upgrade the system to add detectors for future projects if desired?
9. Who will be using the system? (e.g. technicians, students, multiple research teams/projects, single research group)
10. What is the budget?

The first seven questions require clear definition and analysis of the application. Specification of the wavelength range is fairly straightforward. In certain cases when multiple samples may be studied, the user may need to initially accept a lower spectral range, with the intention of extending the range in the future.

Definition of the required spectral resolution is fairly straightforward, but may determine whether or not it is possible to use a CCD or multichannel detector. For applications with relatively low spectral resolution requirements, greater than several angstroms, in the spectral range below 2 microns, a multichannel detector will probably be a good option. But, for higher resolution, careful calculations must be performed to ascertain whether pixel size will limit the spectral resolution. It is not always possible to achieve the required resolution of a MCD system by increasing the dispersion (by increasing the grating groove density, increasing the focal length of the spectrometer, or both), especially when considering the required spectral range. Thus, effective slit widths that are smaller than typical pixel sizes are required. In cases where additional dispersion can not compensate for the size of the pixels, a SCD behind a narrow slit will often yield the required resolution.

As for SCDs versus MCDs, as a general rule, when multiple wavelengths bands need to be measured, MCDs offer faster data acquisition or superior signal to noise compared with SCDs due to the Fellgett multichannel advantage - namely that instead of measuring one

Feature Article The Role of Detectors in Spectroscopy

wavelength band at a time, you can measure multiple bands for the same amount of time. Their tradeoff is cost and complexity. For single or a small number of wavelength bands, SCDs can offer optimum performance at a lower cost. Also, for certain temporal requirements, such as sub 100s of picoseconds, an SCD is the only option. Similarly, the choice of array detectors for wavelengths greater than 2 microns is very restricted and includes few, if any, practical options.

The answer to the fourth question should also be straightforward: if the application involves time-resolved measurements certain detector choices may be eliminated, although the specific technique must still be defined.

The fifth and sixth questions can often be answered by doing preliminary literature investigation of the sample to be studied. Low light level measurements require a detector with high sensitivity and gain, and the capability for long exposure times. The background signal level in the entire spectroscopy system must also be considered. A fragile sample cannot be studied using a detector requiring a long exposure time, so either some type of CCD or PMT with photon counting may be a good choice.

The seventh question requires a good deal of thought. Since the image of the light at the entrance of the spectrometer is projected onto the monochromator exit, the size and shape are important to consider. If a 6 mm tall linear fiber bundle (6 fibers) is mounted at the entrance slit, the detector at the exit should be tall enough to capture all of the photons. An avalanche photodiode with 50 micron diameter mounted directly at the exit slit will not work well, although a PMT with an 8 mm diameter photocathode will be fine. A 2 mm diameter photodiode mounted in a housing containing an elliptical mirror (6x de-magnification) will work well. If the application requires the capture of 6 spectra (one from each fiber) simultaneously, a 2D CCD is required.

The remaining questions require the user to consider the robustness of the detector, whether the housing and mounting hardware will allow additional detectors to be added or substituted, and the amount of daily upkeep and care that is required.

Conclusion

The detector is an integral part of any spectroscopy system. It is not merely an accessory, yet nor does the detector alone determine the performance of the total system. Choosing the best possible detector maximizes the potential of the system as a whole to achieve optimal sensitivity, dynamic range and signal to noise ratio for the application. This principle applies whether using a spectrometer with a single channel detector or a spectrograph with a multichannel detector. As new materials and technologies are developed, new types of detectors will continue to become available. The team at Horiba Jobin Yvon is prepared to test and integrate new types of detectors to keep up with ever more demanding requirements of emerging applications and more challenging measurements using optical spectroscopy.

References

- [1] Donati, S., *Photodetectors: Devices, Circuits and Applications*, Prentice Hall PTR, Upper Saddle River, NJ, 2000.
- [2] Janesick, J.R., *Scientific Charge-Coupled Devices*, SPIE Press, Bellingham, Washington, 2001.
- [3] Janesick, J.R., *Photon Transfer*, SPIE Press, Bellingham, Washington, 2007.
- [4] Adar, F., Atzeni, S., Gilchrist, J., Goldstone, L., Noonan, J., *Laser Focus World*, Vol 38, Number 4. 7.
- [5] ASTM Standard E2642-08, *Standard Terminology for Scientific Charge-Coupled Devices (CCD) Detectors*, ASTM International, West Conshohocken, PA, 2008.



Salvatore H. Atzeni

Vice President
Optical Spectroscopy and CTO
HORIBA Jobin Yvon Inc.
Ph. D.



Linda M. Casson

Senior Application Scientist
HORIBA Jobin Yvon Inc.
Ph. D.