Modern UV-VIS Spectroscopy: A Decade of Fiber-Optic CCD Array Spectrophotometers

by Jeff Prevatt

Ultraviolet-visible (UV-VIS) spectroscopy continues to be one of the core disciplines practiced in nearly every analytical laboratory. Since its inception by Cary and Beckman in the 1940s, UV-VIS spectroscopy has revolutionized the field of molecular spectroscopy. Over the decades, numerous improvements have been made with respect to optical designs, including dual-beam optics, variable slit resolution, noise suppression, and integrated electronics.

The proliferation of personal computers in the 1980s resulted in significant improvements in data acquisition and instrument control. Streamlined instrument operation was facilitated through the use of dedicated software applications and the introduction of the user-friendly Windows™ operating systems (Microsoft, Redmond, WA). Perhaps the most radical instrument design change that took place in the 1980s was the introduction of the diode array spectrophotometer by Hewlett-Packard, now Agilent Technologies (Palo Alto, CA). In contrast to traditional scanning monochromators that utilize a single photomultiplier tube, this novel spectrograph consisted of an array of photodiodes that permitted simultaneous, full-spectrum data acquisition in seconds. It was an instant hit among users.

The 1990s introduced two significant design additions in the form of charge-coupled device (CCD) array detectors and fiber-optic sampling devices. Figure 1 demonstrates a variety of linear CCD sensors available during the last decade. The typical CCD exhibits very high quantum efficiency and has readout noise that is 100 times lower than comparable photodiode arrays, permitting more efficient utilization of light and an improved signal-to-noise ratio. The use of fiber optics allowed the overall optical footprint to be more compact and thus reduced instrument size. In addition, fiber-optic sampling accessories could be configured for use as probes, making possible numerous, untypical spectroscopic applications such as colorimetry, radiometry, and spectroscopy of solid surfaces.

A quick glance at today's instrumentation market indicates the popularity of the CCD as the detector of choice. CCD array systems now dominate almost every product line, including nearly all inductively coupled plasma (ICP) spectrometers (atomic spectroscopy) and IR-Raman (molecular spectroscopy) systems sold. These charge-transfer devices (CTDs) are composed of CCD, charge injection device (CID), and complimentary metal oxide semiconductor (CMOS) array systems. The overwhelming benefits of either array type are simultaneous, multiwavelength data acquisition resulting in the fastest, most versatile instruments available. Additionally, CTD array systems have few, if any, moving parts and offer better stability than single-element, vacuum tube detectors such as photomultiplier tubes (PMTs).

Figure 1 The relative size of linear CCDs arrays used in spectroscopy applications is contrasted against the roll of film they have come to replace in recent years.

Figure 2 High-sensitivity, low-noise, 3648-pixel linear CCD array used in the 400 Series spectrophotometers (S.I. Photonics, Tucson, AZ).

Detector options

The optical design and footprint of CCD array spectrophotometers differ considerably from typical scanning spectrophotometers. The larger footprint required for scanning spectrophotometers can be attributed to the increased number of optical surfaces necessary for dispersion and isolation of the desired wavelength prior to transmission through a given sample. In addition, numerous moving parts are necessary for performing scanning functions, slit selection, and beam splitting. In contrast, CCD array spectrophotometers transmit all wavelengths through the sample prior to wavelength isolation. The use of a fixed grating position results in a linear spectrum that is ideally suited for linear CCD arrays and eliminates moving parts within the spectrograph. Fewer moving parts result in improved reliability, thus minimizing instrument maintenance costs and the necessity for service. Figure 2 depicts a typical linear CCD detector.

Photodiode arrays typically utilize linear arrays consisting of 512 or 1024 photosensitive diodes. In comparison, the most common linear array CCD format currently used is a 2048-pixel CCD. High-sensitivity, low-noise CCDs having either 2048 or 3648 pixels are used in high-performance spectrophotometers offered by S.I. Photonics.

The resulting resolution of an array spectrophotometer is determined by the slit width, dispersion, and pixel binning. Because wavelength dispersion does not incorporate an exit slit, order-sorting filters are essential for linear CCD array UV-VIS spectrophotometers. Improved long-term precision and wavelength accuracy are achieved in CCD array systems by precise temperature control of the spectrograph optics. Fewer optical components result in a smaller spectrograph that can be temperature-stabilized to minimize expansion and contraction of optical components due to changes in ambient temperatures. Typical scanning instruments often have a relatively large optical footprint and do not lend themselves to affordable temperature control of optical components.

Light sources

Typical light sources utilized in UV-VIS spectroscopy include a quartz tungsten lamp for visible wavelengths from 350 to 1000 nm, while deuterium lamps are used for UV wavelengths below 350 nm. Xenon lamps have been used in less expensive systems but do not offer the light throughput, stability, or flexibility of dedicated deuterium and tungsten sources. For the highest performance when choosing an instrument, regardless of scanning or CCD array types, users should look for units that have separate, dedicated light sources.

Fiber optics

When fiber-optic capable systems were first introduced, many critics cited solarization of the optical fibers and photooxidation of samples as potential weaknesses of array spectrographs. These two myths were quickly dismissed since solarization-resistant fibers are typically used and sample analysis times are too short for photooxidation to occur.

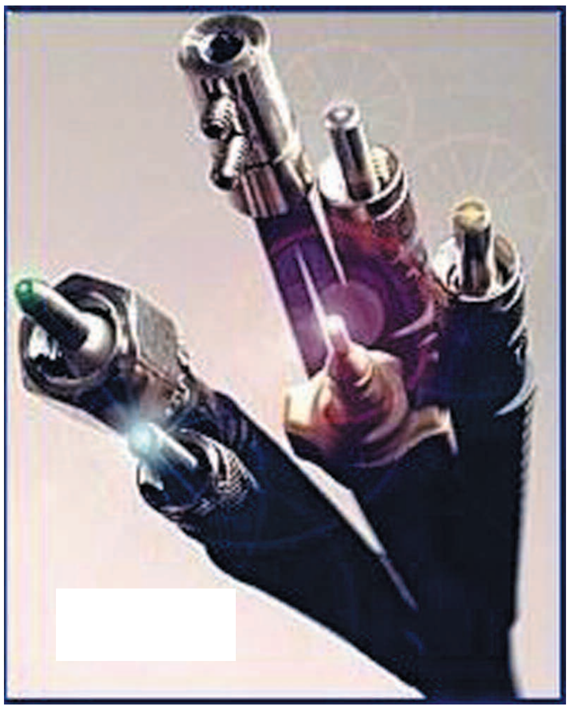

Figure 3 Fiber-optic connectors can be configured to meet any user specifications.

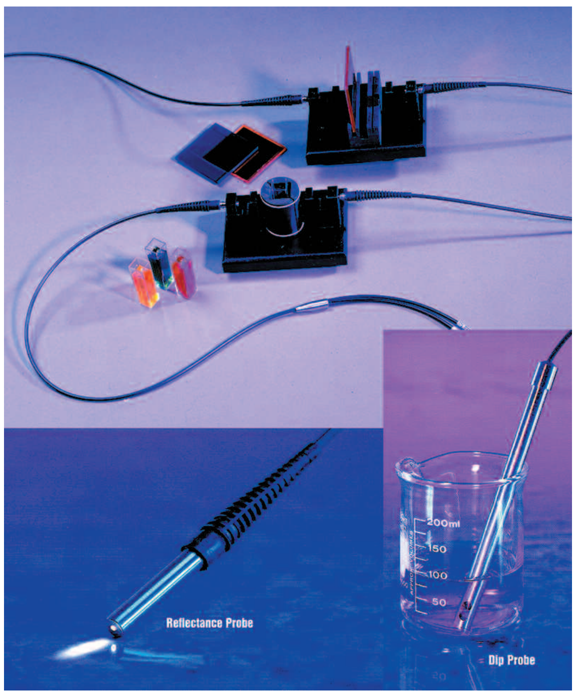

Figure 4 Various fiber-optic sampling options are available for accommodating a variety of sample applications.

In addition, these effects are virtually eliminated in high-quality optical designs incorporating optical shutters. The optical shutters used in the 400 Series spectrophotometers precisely control the exposure of light to the fiber-optic devices down to fractions of a second. As a result, the solarization that would normally occur during the first 10 hr of use would require the performance of more than 35,000 analyses before effects are realized. If the optical shutter happens to be positioned prior to sample illumination, photo-oxidation is eliminated entirely.

Sampling options

The sheer number of applications for the modern UV-VIS system is limitless. New uses are routinely discovered and implemented as a result of the versatility offered by the numerous fiber-optic sampling accessories. For example, traditional UV-VIS spectroscopy was limited to liquid matrices utilizing the standard 1-cm cuvettes. The flexible fiber-optic systems available today have introduced UV-VIS spectroscopy to an entire generation of new users. Dip probes now account for more than half of the units sold rather than traditional cuvettes. Fiber-optic reflectance probes allow for the sampling of solid surfaces and powders as well as aqueous matrices. When true diffuse reflectance is needed, integrating spheres are readily accommodated. Today's systems serve users in scientific research, academic teaching, corporate and industrial QA/QC, pharmaceuticals, radiometry, colorimetry, criminal investigations, and agricultural applications. Figures 3 and 4 depict standard fiber-optic terminals and sampling accessories.

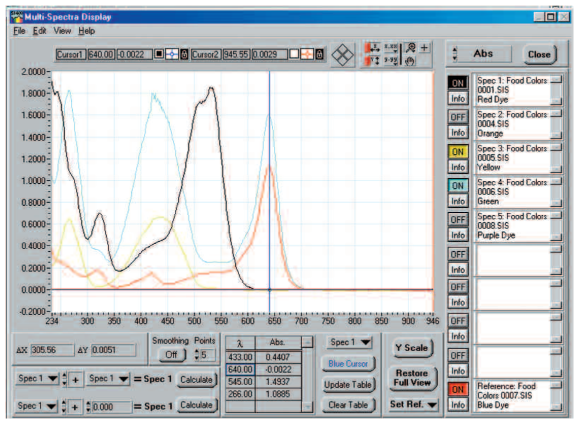

Figure 5 Multiple spectra display panel.

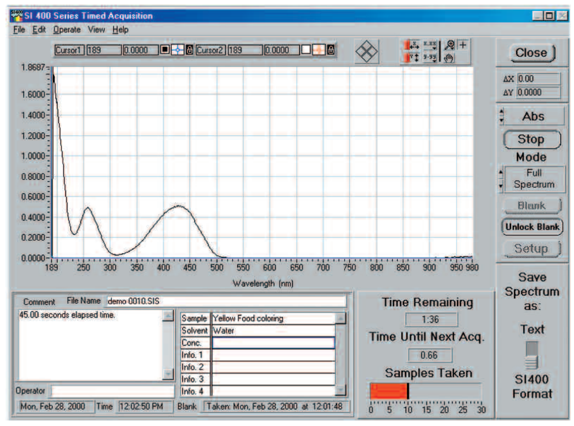

Figure 6 Full-spectrum timed acquisition.

Software

CCD array spectrophotometers have the inherent benefit of software flexibility. Because the entire spectrum is made available instantly and stored in memory, these data can be evaluated repeatedly in a number of fashions. Peak location, quantitation, multiple spectrum overlay, and timed acquisition are typical features included and are indicated in Figure 5.

Timed acquisition

Timed acquisition and kinetics analysis are just two of the applications in which CCD spectrophotometers overwhelmingly outperform scanning systems. Simultaneous, full-spectrum data acquisition offers significant advantages over monochromatic systems, which severely limit data acquisition. Typical CCD spectrophotometers have integrated software capable of displaying spectra as a function of time (Figure 6). As a result, users can choose to view the entire wavelength region over time or simply select discrete wavelengths for temporal studies. These features are extremely valuable for chromatographic applications and fraction collection. Full-spectrum acquisition not only allows for confirmation of the parent compounds, but contaminating artifacts are also identified in real time. These data can then be presented as a three-dimensional plot, providing a powerful tool for drug and metabolite screening and other applications. Kinetics and dissolution testing are also widely used timed acquisition features.

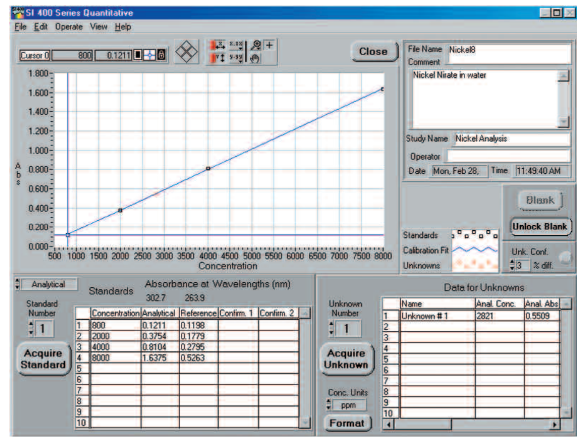

Figure 7 Quantitative analysis panel.

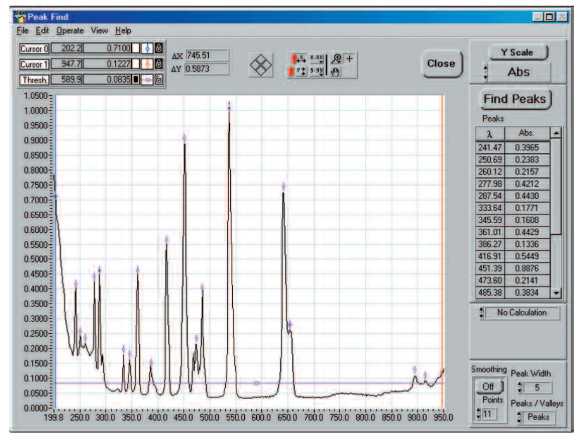

Figure 8 Easy-to-use peak identification.

Quantitative analysis

A significant advantage of CCD array systems over conventional scanning systems is that an array system allows for simultaneous background correction at user-selectable locations. Background correction is not available with single-channel scanning systems, which can only monitor one wavelength at a time. In addition, quantitative analysis can be performed at multiple wavelengths simultaneously, as shown in Figure 7.

Conclusion

The CCD array spectrophotometer of today represents the technological maturation of traditional UV-VIS spectroscopy. These systems are more versatile, reliable, and compact than ever before. Continued advances in software usability make qualitative identification effortless, as shown in Figure 8. In addition, the flexibility afforded through the use of fiber optics and CCD detection has introduced UV-VIS spectroscopy to a new generation of users and applications. New systems incorporating Peltier-cooled CCDs for improved fluorescence applications and dual-beam designs are sure to follow.

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