Howard Cary launched Applied Physics Corp. (later known as Cary Instruments) in 1947, releasing the first commercial recording UV-VIS spectrophotometer, the Cary 11, only a year later. His philosophy, performance combined with flexibility, was a simple one that, fueled by a desire to provide cutting-edge scientific researchers with cutting-edge instrumentation, led to the release of the first commercially available high-end UV-VIS-NIR (near-infrared) spectrophotometer, the Cary 14, in 1954. The opening paragraph of his landmark U.S. patent application of the same year made his intentions abundantly clear: “This invention relates to photometry, and various optical components (or external optics) are also necessary to transfer the light from the source, to the sample, and finally to the detector. In recording (or scanning) spectrophotometers, a double-beam design is generally used to permit measurement with continuous change in wavelength. In this type of instrument, both a sample beam and a reference beam (blank) are monitored continuously, so that absorbance (or transmittance) can be calculated at each wavelength. In this way, source fluctuations and drift are also minimized.

From a design perspective, a spectrophotometer is a complex combination of optics, mechanics, and electronics engineered to give high photometric performance over a particular absorbance and wavelength range. Photometric performance is determined by a number of factors, but is largely dependent on the monochromator—the heart of any spectrophotometer. A monochromator consists of an entrance slit, a dispersion device such as a grating or prism, and an exit slit. Ideally, it produces monochromatic light; however, in practice, a band of light is always produced. A second monochromator can be used to further enhance performance by allowing increased light throughput, reducing aberrations, and providing low stray light levels.

Double-beam spectrophotometers are operated using a beam separated in space or a beam separated in time. The former involves splitting the beam between sample and reference with detection achieved using two matched detectors. The latter employs an optical chopper system to alternate the source between sample and reference. It is generally accepted that chopper-based systems exhibit the higher accuracy of the two, due mainly to the requirement that the detectors be perfectly matched in the first instance. As such, the majority of high-end spectrophotometers are based on the double-beam principle (Figure 1).

Thus the aims of high-performance UV-VIS-NIR spectrophotometer design are fourfold:

- A stable, broad-band source provides the high radiant power necessary over the wavelength region of interest
- A monochromator system provides wavelength scanning and the high resolution, high light throughput, and low stray light required for accurate and precise absorbance measurements
- A low-noise, high-sensitivity detection system offers photometric accuracy and stability over the wavelength range measured
- The external optics efficiently transfer light, splitting it into sample and reference beams, focusing these beams in the sample compartment, and then refocusing them onto the detector(s).

Engineered correctly, the result is a spectrophotometer that displays all of the hallmarks of a high-performance instrument (Figure 2). Key differentiators include spectral resolution, wavelength accuracy and precision, photometric accuracy and precision, low stray light and noise, high stability, and wide linear dynamic range. At the forefront of current spectrophotometer design, and winner of the Scientific...
Commerical and Instrumentation 2002 Reader’s Choice Award for Spectroscopy Systems, the new-generation Cary UV–VIS–NIR spectrophotometers combine the renowned Cary design philosophy with the latest in mechanical, electrical, and optical engineering.

At the leading edge

Redesigned from the ground up, the spectrophotometers incorporate the most recent advances in hardware, firmware, and software. Only the Cary optical layout, designed for high light throughput and optimum sample compartment beam geometry, has been retained in the form of the original optics casting. The new design features PbSmart™ and InGaAs detector management for increased sensitivity and flexibility into the NIR.

The Optical Isolation System shields the monochromator from external influences, guarding against mechanical, electronic, and atmospheric interferences. To minimize vibrational noise, the stiffened optics casting is coupled to a vibrationally isolated mounting system, and floats independently of the spectrophotometer cover and sample compartment. Engineered to meet U.S. military specifications, the internal instrument covers improve grounding and substantially reduce electronic and electromagnetic interference. In conjunction with a sealed and purgeable optics path for reduced risk of atmospheric contamination, the heart of the spectrophotometer is completely isolated from external influences. Internal vibration reduction further complements the Optical Isolation Sys-
tem, providing extremely low noise spectrophotometry.

Powered by the latest generation of fast microprocessors, new detector control algorithms intelligently optimize the performance of the PbS NIR detector in real time. This affords a significant improvement in noise and linearity performance from this mature detector technology, and takes PbS detector performance to a new level. Combined with the latest in Peltier thermoelectric cooling, this approach provides very high performance across applications as diverse as quantifying the out-of-band blocking characteristics of bandpass filters and measuring the high transmission of next-generation fiber optic materials.

Flexibility and responsiveness, or functionality

In keeping with the company’s tradition of providing application-specific solutions, the world’s first InGaAs double-beam UV-VIS-NIR spectrophotometer was developed with demanding photonics and telecommunications applications in mind. This pioneering work aimed to take advantage of the dramatically reduced noise and improved sensitivity of the InGaAs detector in the NIR (up to 1800 nm). Now in its second generation, the InGaAs detection system provides excellent signal-to-noise performance. The low noise and high sensitivity of the InGaAs detector system are further enhanced by the Cary Optical Isolation and Peltier detector cooling systems, and result in improved detection limits and increased scan rates, giving cleaner spectra with better resolution in less time.

The spectrophotometers can also provide photometric performance in the deep UV spectral region down to 140 nm. Developed specifically for use by the semiconductor industry, the instrument is well suited to measurement at the laser wavelengths currently used in integrated circuit (IC) manufacturing processes (248.4, 193.4, and 157.6 nm). The research-grade, double-beam, deep-UV spectrophotometer breaks the vacuum UV barrier for the characterization of silicon wafers, photoreists, and microlithography optical components such as stepper optics, allowing transmission and reflectance measurements from 140 to 260 nm. Combining sampling flexibility with high performance, the Cary deep-UV spectrophotometer is suitable for both deep UV metrology and R&D.

High performance

Photometric linearity determines how accurately a spectrophotometer measures absorbance with increasing optical density or concentration. If an instrument has poor linearity, calibration curves may deviate from linearity at high absorbance levels, reducing the photometric range of the instrument and accuracy of high optical density measurements. The “addition of filters” technique provides a straightforward means of demonstrating the photometric linearity and range of a spectrophotometer. The addition of two blue filters (Figure 3) shows the wide photometric range and linearity of new-generation Cary spectrophotometers in the UV-VIS (>9 abs). The inset in Figure 3 compares the sum of the two filters measured individually with the spectrum of the two measured together, and shows a difference of less than $8 \times 10^{-8} \%T$ between the two.

Along with linearity, photometric accuracy defines the ability of a spectrophotometer to measure an absorbance that can be directly related to a standard solute of known concentration. Photometric accuracy and linearity are vital wherever quantitative measurements are concerned, since the ability to measure the correct photometric response for a given concentration is essential for any analytical measurement. Of similar importance is the range over which the spectrophotometer remains linear. This is known as the linear dynamic range and is defined as the concentration range over which absorbance and concentration remain directly proportional to each other. A wide linear dynamic range permits the measurement of a variety of sample concentrations (optical densities) and reduces sample preparation (dilution) requirements. The quantitative analysis of aqueous potassium permanganate (Figure 4)
further demonstrates the photometric accuracy and range of the spectrophotometers. Measurement at 555 nm permits determination from 0.1 to 500 ppm without dilution, and the plot of absorbance versus concentration highlights the wide linear dynamic range ($r^2 = 0.999$) of the instruments.

Permitting measurement in excess of 8 abs, the spectrophotometers are capable of measuring the most challenging samples. Whether collecting kinetics data in situ without dilution, or measuring turbid, highly scattering life science samples without the need for an integrating sphere, the spectrophotometers deliver the performance and flexibility required. Their wide photometric range accommodates the highest optical density filters and the lowest reflectance antireflection (AR) coatings, while the inherent linearity and dynamic range of the instruments ensures analytical accuracy and eliminates the need for unnecessary and time-consuming sample and standard dilutions.

The next generation

For more than half a century, the Cary name has been synonymous with high-performance spectrophotometry in the ultraviolet, visible, and near-infrared regions of the electromagnetic spectrum. The fact that an early Cary makes its home at the Smithsonian Institute in Washington, DC, bears testament to the role played by Howard Cary in the development of modern analytical instrumentation. Contributions from subsequent generations of scientists and engineers have ensured that Cary spectrophotometers have become the benchmark for performance, flexibility, and reliability in this field. The new generation of Varian Cary spectrophotometers continues in the same vein, providing the performance necessary for those pushing the edge of technology with their measurement requirements.

The spectrophotometer series enables a wide variety of physical and optical measurements. A versatile sample compartment and accessory range permit a wide range of sample types, and very high optical performance enables measurement at the highest limits of performance. From solids and liquids to gases; from powders to films to wafers; from the smallest, high-technology optical filter at the center of a laser guidance system to large sheets of glass for skyscraper windows, the spectrophotometers provide the versatility and flexibility demanded by diverse applications requiring the ability to analyze a vast array of sample types using a wide variety of techniques.

In the words of Howard Cary, “For investigators who on occasion must push a spectrophotometer to the very limits of its performance capability to obtain the information they need, and yet have an instrument that is adaptable to many different applications,”3 Cary spectrophotometers are the natural choice.

References


Figure 4 Quantitative analysis of aqueous potassium permanganate.