Spectrophotometry on the Rise

Kimberly S. Cleaves

Convenience and portability make UV–vis the ultimate laboratory tool.

The sentiment at Pittcon in 1999 was that "the lack of breakthroughs in spectrometry technology at the visible (vis) or ultraviolet (UV) wavelengths can be interpreted as evidence either that the most cogent properties of matter in instrumental analysis have been used (the "no new worlds to conquer" point of view) or that analytical chemists realize that much more can be done with the capabilities we already have" (*1*). Since then, the technique has enjoyed a renaissance, the time-honored UV–vis spectrophotometer has been "rethought, refurbished, and redesigned to remain a vital and growing part of modern science," according to Mark Lesney of *Today's Chemist at Work*, and researchers are increasingly using these cleverly manufactured instruments and taking advantage of their wide spectrum of features. The resurgence of this technology has been sparked largely by its applicability in enhancing pharmaceutical applications but it remains a critical analytical instrument in fields ranging from biotechnology to environmental chemistry.

The technique of UV–vis spectrophotometry has long been a universal laboratory tool, used both in benchtop instrumentation (the familiar UV–visible spectrophotometer) and as a detector for various analytical techniques used by chemists and scientists in related fields (*2*). Some applications of UV–vis technology include HPLC, high-throughput visible colorimeters for clinical analysis, and portable water analysis equipment used in environmental chemistry. In a field where turn-around time, sample size, and integrity are crucial factors, UV–vis is a simple method that provides rapid results in a nondestructive format where sample remnants can be used for further analysis by other applications.

Across the Spectrum

Whether for quantitation of a protein or confirmation of a compound's identity, in the past few years, UV–vis spectrophotometry has increasingly been applied in new and different fields (*3*). Since the inception of spectrophotometry at the beginning of the 20th century and the introduction of the Beckman DU UV–vis spectrophotometer in 1941, optical instruments have gone from being immoderate specialized equipment to inexpensive and routine. Although today's instruments are significantly different from the DU model, they all operate on the same basic principles and have consistently contributed to technological advances in spectroscopy in mainstream and niche applications, such as hyperspectral imaging.

PHOTO: PHOTODISC

Recently, a Strategic Directions International report (*www.strategic-directions.com*) on process spectroscopy use in the life sciences market found that while some commonly used types of spectroscopic instrumentation have seen moderate growth, several methods will benefit from recent advances in technology, such as UV–vis. This is also true for environmental applications, where scientists are capitalizing on its ability to quickly provide data in remote field applications.

The resilience and evolution of UV–vis spectrometry in applications used to monitor and analyze pharmaceutical and biotechnology processes and aid in environmental remediation have demonstrated that chemists are embracing the practice of doing more with existing capabilities.

Not Just for the Lab

By taking advantage of scientific breakthroughs in UV–vis spectral research, scientists have developed techniques to detect and identify environmental contaminants by hyperspectral spectroscopy. And increasing interest in hyperspectral spectroscopy remote sensing has led to a pioneering adaptation of the technology in the environmental chemistry field. Researchers are able to read the spectral images, decode their characteristics, and apply this technology to developing programs that determine how samples are accessed in the field.

This emerging technology integrates the spectrophotometer with systems that collect and provide unique reflectance signatures of materials that help produce maps in real time. Considerable research is being conducted in spectral sensing, and scientific advances in this area are opening the door to new technological opportunities for geologists.

The Mechanics

Spectral imaging is being applied by geologists working in California's Sierra Nevada foothills to characterize historically mined volcanogenic sulfide deposits in abandoned mines. The researchers are analyzing stream and river water to detect modifications induced by salt deposit precipitates. According to Tina Takagi of the University of California–Berkeley (*www.berkeley.edu*), the mines range from those free of environmental problems to those that clearly produce damaging acid mine drainage and require cleanup. The researchers use UV–vis to classify the mines in a timely manner and assess the need for remediation (*4*). In 2000, a research team led by Takagi was equipped with a global positioning system (GPS), laser digital mapping apparatus, computer, and portable UV–vis-NIR spectrophotometer, and they mapped geolocated reflectance data of predetermined sites in the Sierra Nevada foothills.

The presence of metals and their species are two of the most important factors to be determined in water chemistry for mine characterization. Also critical is the search for new mining resources, which requires the development of fast and moderate-cost analytical methodologies for the multi-elemental determination of as many elements as possible in a single sample (*5*). An integrated method involving periodic water sampling, UV–vis-NIR spectroscopy analysis, and digital mapping has been shown to "provide a rapid method for identifying the various oxide, sulfate, hydroxide, and oxyhydroxide minerals that precipitate on mine dump surfaces," allowing scientists to interpret their presence chemically, Takagi explains.

Overcoming Challenges

Although it is known that abandoned mine sites affect watershed chemistry, the challenge for Takagi's team was to determine the extent of downstream precipitates of mine runoff on river chemistry. Classic geochemistry methods are effective for mapping and surveying mine sites but do not effectively identify acid indicator minerals or afford flexibility in the field. Additionally, high-altitude remote-sensing methods lack the spectral and spatial resolution to resolve the presence of indicator minerals.

The climate of the foothills and the high pyrite content of volcanogenic sulfide deposits influence the physical properties of area river water. "Pyrite in the mining waste rock of the old mine dumps oxidizes, releasing metals and acid into solution," said Takagi. After the pyrite in the solution is carried to the mine dump surface via seepage or capillary rise through subsequent evaporation, the physicochemical changes that occur in the solution cause the formation of soluble salt minerals. The researchers observed that mine dump surface mineralogy and mineral distributions varied with physical disturbance and season, and that the resulting sampling was dependent on the surface environment at the time.

To characterize minerals located in the mines and improve the efficiency of identification and mapping, Takagi's colleague Irene Montero developed a method called fast mineral identification (FSTSpecID) using an algorithm for reflectance spectra for identifying minerals that exhibit absorption features in the 0.35–2.5-µm range (*6*). The researchers used the FSTSpecID method to analyze field-acquired samples that contained intensity of reflected light as a function of wavelength. Spectral identification, by UV–vis spanning the ultraviolet, visible, and near-infrared light with a spectral resolution under 0.03 µm, was confirmed by comparing the adsorption centers as well as absorption features of iron minerals to reference spectra in the FSTSpecID library.

Hyperspectral reflectance spectroscopy—reflectance with many adjacent narrow bands—of the samples detected secondary iron minerals formed as a consequence of the oxidation of pyrite above the water table. These samples exhibited absorbance spectra that yielded distinctive patterns that were used to identify the mineral presence and the environment in which they were formed. Favorable correlations were found between spectral reflectance and reference data for copiate, jarosite, goethite, ferihydnite, and hemate, secondary minerals that form from the oxidation of iron sulfide deposits. In iron sulfates, oxyhydroxide and oxide characteristics are displayed in two regions that allow for mineral identification, referred to as NIR and near-UV.

Not Your Typical Application

UV–vis spectrophotometers are used in a vast array of industries and applications, including chemistry, toxicology, biochemistry, clinical chemistry, and materials science, as well as the electronic, semiconductor, pharmaceutical, food, and water industries.

In an environment where the pace of technology is rapidly advancing, the spectrophotometer offers scientists a rapid, effective, and inexpensive method of analysis, and in some applications it has been purposed for catalytic processes. Although "the catalysis industry has been working nanoscale for more than 40 years," according to Bing Zho, head of catalyst research at Hydrocarbon Technologies in Lawrenceville, NJ, "the recent application of UV–vis technology by Alexis T. Bell and Enrique Iglesia of the University of California–Berkeley led to the indirect measuring of catalyst particle sizes," subsequently affecting the reaction rate.

Likewise, UV–vis has become an important technique used in the oxidation of organic pollutants in water that are not easily removed during wastewater treatment. The combination of UV–vis and solar-driven power allows degradation by photocatalysis.

Where to Next?

The UV–vis-NIR combination offers a portable and definitive method of identification of minerals using reflectance spectra. The ability to perform rapid analyses and discover reflectance patterns inherent in hyperspectral data collecting is becoming more important to researchers in the field. Using an algorithm in combination with GPS and a geographical mapping system, Irene Montero adds that "the characterization of the shape of absorption features in the reflectance spectrum is a definitive way to identify minerals from their reflectance spectra, even in the uncontrolled, complex environment of abandoned mines."

A better understanding of the effect of atmospheric conditions on spectral imaging, and the behavior of these conditions in various environments, is essential to interpreting hyperspectral imagery. By identifying and interpreting spectral data, the Berkeley scientists have established a method of characterizing mines in the field. Currently, these collections are helping the researchers to integrate a noninvasive approach to identification using low-altitude remote-sensing applications to enhance their spectral libraries.

References

(1) Lesney, M. S. *Today's Chemist at Work*, April 1999, 39–41.
(2) Dadd, A.; www.product-search.co.uk/internationallabmate.com/features/oct2000/spectrophotometry.shtml.
(3) Beck, S. *The Scientist* **1998,** *12* (3), 20.
(4) Takagi, T.; Brimhall, G.; http://eps.berkeley.edu/groups/erc/Documents/takagi.pdf.
(5) de la Guardia, M.; Garrigues, S. *Trends Anal. Chem*. **1998,** *17* (5), 263–271.
(6) Montero, I.; Brimhall, G.; http://eps.berkeley.edu/groups/erc/Documents/montero.pdf.

Kimberly S. Cleaves *is an associate editor of* Today's Chemist at Work. *Send your comments or questions about this article to tcaw@acs.org or to the Editorial Office address on page 3.* ◆