Diode arrays may light up compact spectrometers

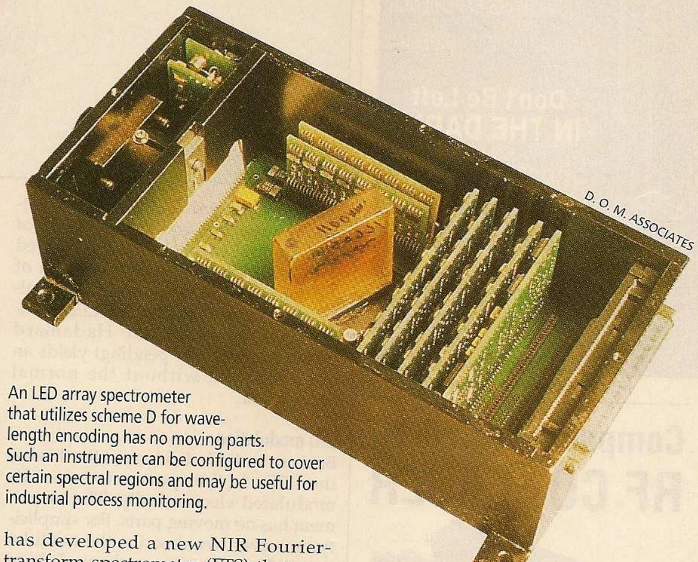
LEDs in arrays may soon serve as light sources in compact, rugged instruments for spectroscopy.

R. Sobczynski, J. L. Porter, R. M. Hammaker, and W. G. Fateley

Since the first reports in 1962 of high electroluminescence from GaAs with *p-n* junctions, spectroscopists have wished to use these light-emitting diodes (LEDs) for the study of physical problems and in particular for work in analytical chemistry. The continuing progress in semiconductor technology, especially in the fabrication of these LEDs, has yielded optoelectronic devices in both the visible and the near-infrared (NIR) spectral regions. Recently, the range of LEDs has been expanded to the mid-infrared spectral region.

Now a very simple spectrometric device can be constructed with only a few LEDs as its source of radiation. For example, the oxygen in the blood of a patient can be monitored by a catheter oximeter that uses two LEDs: one at 685 nm and the other at 920 nm to measure blood oxygen and background, respectively. This application leads to the design of even more sophisticated instruments using an array of LEDs as a single source. The availability of LEDs in the NIR spectral region and the very broad absorption bands that compounds have in this region provide a new analytical application of LEDs to spectroscopic studies. Our company has developed a new NIR Fourier-transform spectrometer (FTS) that uses an array of LED sources and has no moving parts.

The authors are with D. O. M. Associates, 631 Levee Dr., Manhattan, KS 66502. RADEK SOBCZYNSKI is research and development manager, LANCE PORTER is a senior design engineer, ROBERT HAMMAKER is also a professor of chemistry at Kansas State University, and WILLIAM FATELEY is president of D. O. M. Associates and a distinguished professor of chemistry at Kansas State University.



An LED array spectrometer that utilizes scheme D for wavelength encoding has no moving parts. Such an instrument can be configured to cover certain spectral regions and may be useful for industrial process monitoring.

LEDs in NIR spectroscopy

The statement can be made that anything that can be analyzed in the mid-infrared spectral region (5000 to 200 cm^{-1} or 2 to 50 μm) can be analyzed in the NIR spectral region (14,000 to 5000 cm^{-1} or 750 nm to 2 μm). The nature of the NIR spectral region allows high signal-to-noise ratios, choice of radiation sources, and glass and fiberoptic sampling cells and probes. In this region, spectral interference from water is limited and high resolution is not necessarily required. Adequate characterization of samples in the NIR region usually requires only 5-nm resolution.

Even at this limited resolution, gas-phase studies are possible. Gaseous systems such as simple hydrocarbon mixtures—methane, ethane, propane, butanes, and pentanes—have been analyzed for the individual hydrocarbons. The application of multivariant methods such as partial least squares (PLS), principal component regression (PCR), and multiple linear regression (MLR), as well as other mathematical analysis techniques, is necessary to permit use of a low-resolution instrument in the NIR spectral region.

To take advantage of this spectral region with all of its attractive features, a number of commercial instruments have been developed over the past two decades. Our Fourier transform near-infrared (FT-NIR) instrument with LED sources compares well with these other instruments. A narrow spectral region can be selected from the broad-band radiation of an LED by a holographic grating; this bandpass can be 10 to 20 nm wide. The LED radiation can be collected by a mirror or concave holographic grating to create a point source or to couple to a fiberoptic probe.

Detection of the NIR radiation from a sample is a simple task. All the LEDs

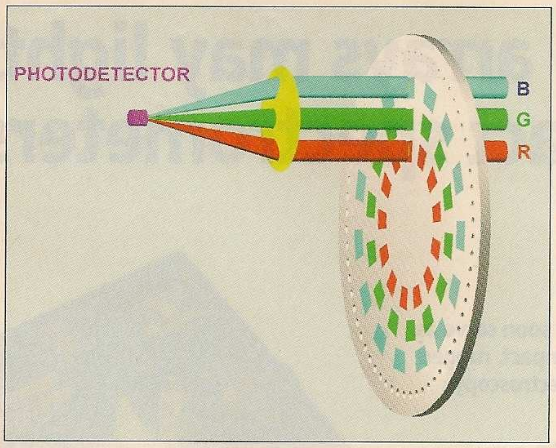


FIGURE 1. Each diode source—B (blue), G (green), and R (red)—impinges upon a different encodement ring in the wheel. These rings with rectangular openings are used to sequentially encode the radiation. The small squares at the periphery of the wheel provide the proper alignment for encodement. The exiting encoded radiation is combined and focused into a detector.

can be modulated at different individual frequencies, and the intensity of each spectral channel can be recovered with a standard Fourier transform of the detected time-domain signal. Finally, adjusting the phase of the LED modulations by a special Hadamard encodement (patent pending) yields an interferogram without the normal center burst.

LED modulation

Because a diode is electrically driven, the LEDs in the spectrometer can be modulated electronically. The instrument has no moving parts. For simplicity, however, we describe the modulation technique as if a mechanical chopper were used. The modulated radiation from each diode is combined to form the radiation source, which is directed to the sample and impinges upon the detector.

Three LED sources are considered here: B (blue), G (green), and R (red) (see Fig. 1). This radiation impinges on a chopper wheel at three different locations. At this point the radiation from a single diode is encoded and the resulting radiation exits from the chopper wheel.

For our discussion, we have chosen four different chopper wheels, each of which yields a different modulation pattern (see Fig. 2). The physical position of each wheel is identified by alignment holes, appearing as circles in the outer portion of the wheel. The angular velocity of rotation for each wheel is held constant. The design of chopper wheel A simulates sequential encoding. For example, the order of LED energies reaching the detector would be B, G, R, B, G, R, and so forth; in this case, a single spectral channel reaches the detector for each measurement.

The second chopper wheel, B, simulates a Hadamard encodement of radiation. This Hadamard encodement follows from a cyclic S_3 encoding matrix.[1] Thus the first measurement, d_1, at the detector receives energy from B + G, the second measurement, d_2, involves B + R reaching the detector, and the third measurement, d_3, is the combination of G + R. The Hadamard transform of the detector signals yield the spectral energy, I_1 of each diode.

The third chopper wheel, C, will modulate the light from the LEDs in such a manner that the three orthogonal modulating frequencies will be beating in the time domain. This signal is the usual Fourier-transform interferogram containing a center burst. Transforming the photoelectric signal recorded at the detector by performing a fast Fourier transform (FFT) will yield the spectral energy of each LED; these energies are usually identified as intensities by spectroscopists.

However, we find that a better scheme for encodement of these three LEDs is illustrated by the fourth wheel, D. The encoding patterns demonstrated in wheel D are similar to the patterns in wheel C; however, upon examination of wheel D, one can see a difference in specific phases for each LED between the colored notches. [The effect of this phasing on the signal generated is left for another paper and patent.[2]] In summary, this encodement scheme eliminates the center burst in the time-domain signal for a FTS (see Fig. 3).

In the latter three modulation schemes, chopper wheels B, C, and D deliver more energy to the detector during each full turn of the wheel than does scheme A. In the nomenclature of Fourier-transform infrared spectrometry, this is called the Fellgett advantage or multiplex advantage. In theory, the signal-to-noise ratio can be increased by a factor proportional to the square root of the number of spectral channels present.

Schemes A and B require the detector to respond to instantaneous changes in signal strength. In practice, this is not possible, and transients in the time-domain signal result. Schemes C and D allow the signal strength at the detector to be varied more steadily, reducing the effects of transients and distortions on the time-domain signal. In addition, schemes C and D allow the signal to be AC coupled, decreasing the effect of $1/f$ noise on the results compared to schemes A and B.

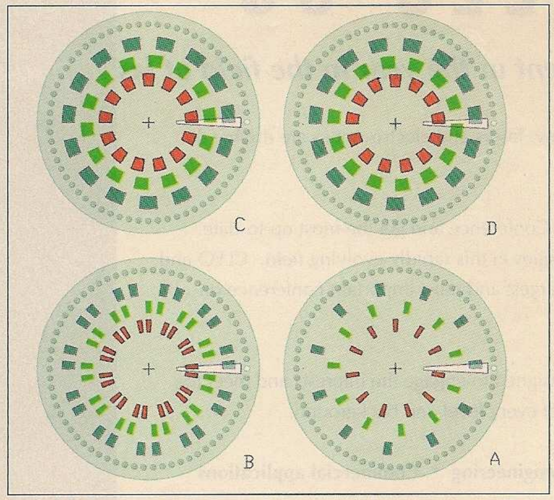


FIGURE 2. Chopper wheel A provides a sequential encodement: B, G, R, B, G, R, ... passing one diode source at a time. Wheel B yields Hadamard encoded radiation. The first sequencing is B + G; then, B + R, G + R, B + G, and so on. Wheel C adds three orthogonal waves to the signal. Wheel D has a similar sequencing as C except the phase of the radiation is Hadamard encoded.

LEDs and temperature

LEDs are less-than-perfect sources of radiation. The intensity of their emitted light tends to vary both with fluctuations in electrical current and with temperature. Typically, the integral light intensity of a LED varies from 0.2% to 0.5% per kelvin (see Fig. 4). To minimize these variations in emitted light with temperature changes, precise temperature control of the diode substrate must be employed.

However, the data in Fig. 4 suggest another approach. Note that there is a narrow band of wavelengths in all three profiles in which the intensity is constant: we have coined the term "isointensitic point" for this region. With a holographic grating, only a small band of wavelengths can be selected from a particular diode, and only this

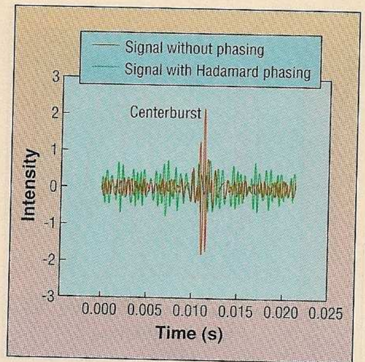


FIGURE 3. Red trace is the interferogram with the characteristic center burst (points of greatest intensity). Time-domain signal with Hadamard phasing encodement of each diode is green. All diode energies are combined and appear on the detector. No center burst is present in the signal with Hadamard phasing encodement.

radiation is allowed to pass. If the diode is designed so that its isointensitic point is selected by the grating, then the emitted intensity is independent of the temperature.

An LED array spectrometer

The hybrid 31-element array of LEDs in our LED array spectrometer is composed of custom LED chips available from D. O. M. Associates (see photo on p. 75). The diodes are arranged in the focal plane of the concave holographic grating and below the optical plane of the grating. Above this optical plane, the radiation collected from the grating will exit. This optical arrangement allows a preselected 12-nm-wavelength optical bandwidth to exit from each LED. The combined radiation emerging from this exit slit is directed to the sample and then detected.

The total spectral range is 150 nm; this instrument covers the 800-950-nm spectral region. Several spectrometer modules have been built to cover the 1000-1750-nm spectral range in 150-nm increments. The modules can be custom-tuned toward specific spectral regions of interest. Sets of concave holographic diffraction gratings made by

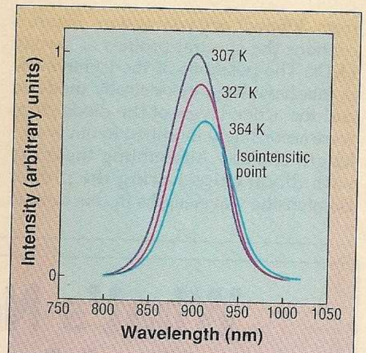


FIGURE 4. Shift in peak wavelength for a single diode follows changes in temperature. At the the isointensitic point, little intensity changes occur with temperature.

American Holographic (Littleton, MA) are optimized to work with the diode arrays in the desired spectral region.

To effectively cover the 150-nm spectral range, three different groups of InGaAsP chips were used. The diode chips in the array were manufactured from different epitaxial wafers. Figure 5 contains the spectral profiles of several LEDs. The positions of the isointensitic points have been theoretically modeled and the active layers of the diode chips were accordingly modified to our wavelength choices. Assembling the array with diode chips having the proper isointensitic wavelengths in this fashion greatly reduces the need for precise temperature control.

The sine-wave LED modulator allows the encodement of each of the spectral channels.[3] The modulation frequencies lie within one octave around 2 kHz. To illustrate the benefits of using the Hadamard phase-encoding scheme, compare the time domain data obtained by the spectrometer in Fig. 3. The center burst is very pronounced if the Hadamard phasing is not incorporated. Proper digitizing of the interferogram requires a large dynamic range. Using Hadamard phasing according to scheme D eliminates the center burst and consequently decreases the dynamic range necessary to digitize the interferogram.

The frequency-domain data show a noise floor of 96 dB below the signal (see Fig. 6). To reach this level of signal purity, the measurement requires less than three seconds of data acquisition. The photoelectric signal was processed by a 20-bit signal processing board and a digital signal processor inside the spectrometer. The instrument shows excellent long-term stability: we have measured better than 1×10^{-4} absorbance units over one hour. The

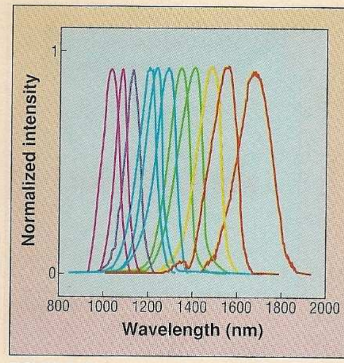


FIGURE 5. Custom manufactured LEDs cover the near-IR region. (All diode intensities are normalized to a value of one.)

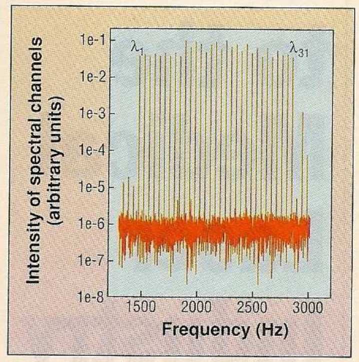


FIGURE 6. Signal from each of the 31 LEDs is phase-modulated to eliminate the center burst when taking the Fourier transform in the time domain. (The 1 e-1 means 1×10^{-1} intensity at a modulation frequency in hertz.)

photometric noise is low, better than 20×10^{-6} absorbance units. The long lifetime of the diodes guarantees low maintenance.

Applications of the new encoding scheme are not limited to LED spectrometers. Other devices such as multiwavelength acousto-optic tunable filters (AOTFs), instruments for ultrasonography, and others can benefit from this invention, as can any situation in which saturation of the dynamic range of the analog-to-digital converter (ADC) can cause a problem. The only requirement for implementation of this encoding scheme is to have control over the signal sources, and LEDs are easy to control. Because the spectrometer modules can be customized for certain spectral regions, it is possible to develop rugged industrial products that can monitor dedicated processes and/or reactions. □

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