Fast-scan spectrometry

Combining electronic and optical techniques and data processing provides a way to apply spectroscopy to studies of fast reactions such as luminescent decay and stopped flow. Here is how these instruments operate, along with some application examples

by Peter Burke
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Spectrometry has become one of the mainstays of science and industry. It provides the ability to measure light intensity as a function of wavelength and thus serves as an accurate technique for studying and controlling chemical and physical processes. The first spectrometer consisted of an entrance slit, a prism, appropriate lenses for collimation and focusing, and the eye for a detector. To observe different regions of the visible spectrum, the prism and focusing lens were moved by hand. Most modern spectrometers still incorporate these same features, although the diffraction grating has tended to replace the prism, the gear train has replaced the hand, and the film plate and photomultiplier tube have replaced the eye. The resulting instruments consist of spectrographs and spectrometers. Spectrographs have large film plates or arrays of photomultiplier tubes and excellent wavelength resolution. Spectrophotometers have dual optical paths and superior differential sensitivity.

What most modern spectrometers have failed to provide, especially those costing less than $10,000, is fast access to the data that they gather. Film-based instruments gather information at many wavelengths simultaneously, but the time required to process and read the film is typically 20 to 60 minutes. Photomultiplier tubes respond rapidly and the result can be read in seconds, but data can be gathered at only one wavelength at a time. For photomultiplier-based instruments to gather information over a range of the spectrum, the spectrum must be scanned by moving the grating and detector over a time span of 2 to 60 minutes. Alternatively, a separate detector for each predetermined wavelength of interest can be provided at an addition in cost of about $500 to $1000 per wavelength.

In response to the need for fast data acquisition, either for convenience or for following rapidly changing events, several fast-scan spectrometers have been developed. Some of these spectrometers still use a single photomultiplier tube for a detector but replace the slow scanning gear train with rapidly rotating or oscillating mirrors and gratings. One of the first commercial instruments, a single-beam spectrometer, rotated a sequence of corner mirrors through an intermediate focal plane of the spectrometer, thus sweeping the spectrum past the exit slit and the photomultiplier tube at rates up to 200 nanometers per millisecond. A more recent spectrophotometer vibrates a mirror to scan the spectrum of an excitation light source past the exit slit of the monochromator. The monochromatized light then passes through a beam splitter and thence to reference and sample cells and photomultiplier tubes. Spectra can be scanned at rates up to 100 nanometers in one millisecond. A low cost spectrocolorimeter based on a rotating filter wheel is also available, scanning 300 nanometers in 50 milliseconds.

Other new spectrometers have shunned mechanical

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means of scanning the spectrum and relied upon electronically scanned image detectors. These detectors include the silicon vidicon camera tube and the line scanner or self-scanned array. The detector in the vidicon consists of a square array of photodiodes, typically 1000 × 1000 diodes. The detector in the line scanner consists of a row of photodiodes, typically 1 × 256 diodes. With both detectors the dispersed spectrum is focused on the front surface of the array. In the vidicon the resulting signal is recovered by scanning the back of the array with a focused electron beam, as in a cathode ray tube, and monitoring the target current. Scan rates of 400 nanometers in 10 milliseconds are achievable. In the self-scanned array, the optical signal is scanned by a clocked shift register that addresses each diode in sequence. The resulting signal is a train of charge pulses, each having a magnitude proportional to the light intensity of the corresponding photodiode. Scan rates of 100 nanometers in 0.5 milliseconds have been achieved. Two commercial instruments based on the vidicon are available but as yet none based on the self-scanned linear array.

Silicon photodiode detectors

The silicon diode array is particularly attractive as the basis of a new spectrometer since it combines some of the advantages of spectrographic film with some of the advantages of the photomultiplier tube. It has enough target resolution elements to permit simultaneous observation of reasonably large portions of the spectrum. The target integrates and stores all optical information coming into it as a pattern of stored electrical charge. The stored charge pattern is converted into an amplified electrical signal suitable for further processing and viewing in times on the order of 10 milliseconds in the vidicon and faster in self-scanned linear arrays. Dynamic optical events on a millisecond time scale can thus be followed. Spectral information about faster events, such as flashes and pulsed light sources on a sub-microsecond time scale, can be captured by the target and then read out in milliseconds.

Silicon photodiode arrays are useful optical detectors over the region of the spectrum in which silicon absorbs photons. This extends from 300 to 1100 nanometers, although silicon detectors with ultraviolet sensitivity to about 200 nanometers are becoming available. Silicon detectors are impervious to damage by high light intensity, have a high quantum efficiency and an output signal linearly proportional to the incident optical flux.

The photodiode array in the silicon camera tube consists of diodes spaced about 15 micrometers apart (Fig. 1). The diodes are biased such that they are nonconductive (reverse bias) and act as capacitors and store charge. The diodes are biased in sequence as the electron beam in the vidicon repetitively scans the target. When the diodes are fully charged, the electron beam can deposit no further charge and thus no signal is recovered from the target. After the diodes are discharged, either by photon-generated electron-hole pairs or by leakage, the electron beam can replenish the charge and current flows through the diode. This current is the vidicon signal and is directly proportional to the number of photons that have fallen on the target.

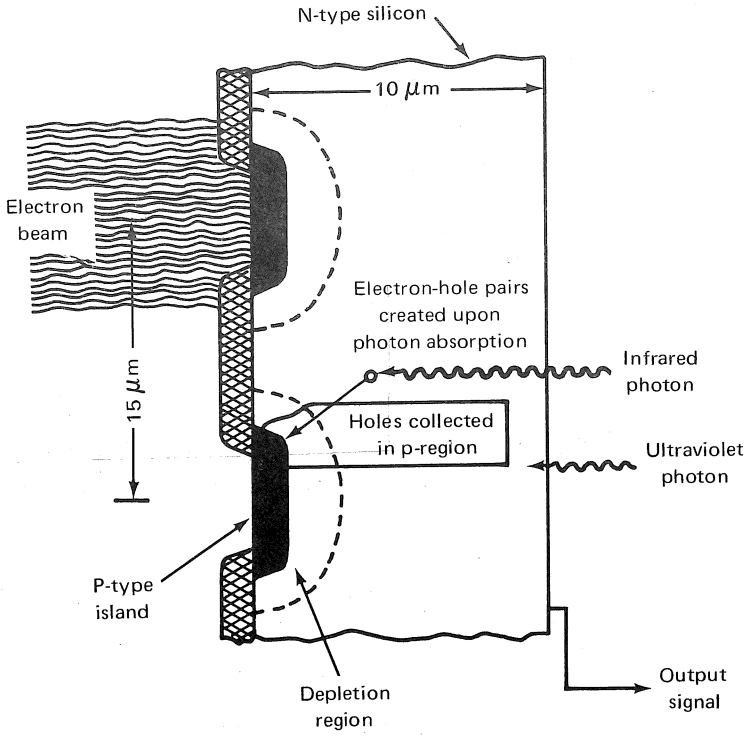


Fig. 1. Detector in silicon vidicon camera tube consists of an array of photosensitive diodes grown on silicon wafer. Diodes are spaced about 15 micrometers apart.

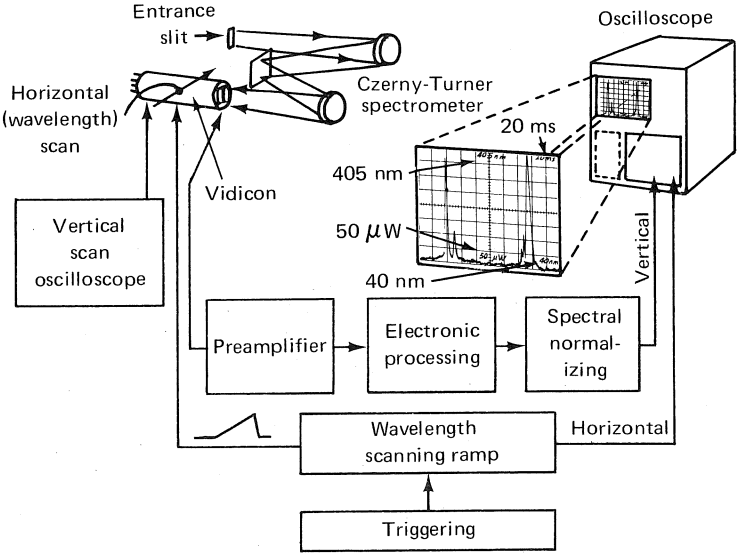


Fig. 2. Rapid-scan spectrometer system (RSS) has three major parts: spectrometer, oscilloscope and an oscilloscope plug-in. System can scan 400 nanometers in 10 milliseconds.

RSS scans 400 nm in 10 milliseconds

The Rapid Scan Spectrometer (RSS) system developed by Tektronix consists of three parts: a spectrometer, an oscilloscope and an oscilloscope plug-in (Fig. 2). It can scan up to 400 nanometers of the spectrum in 10 milliseconds and display the resulting

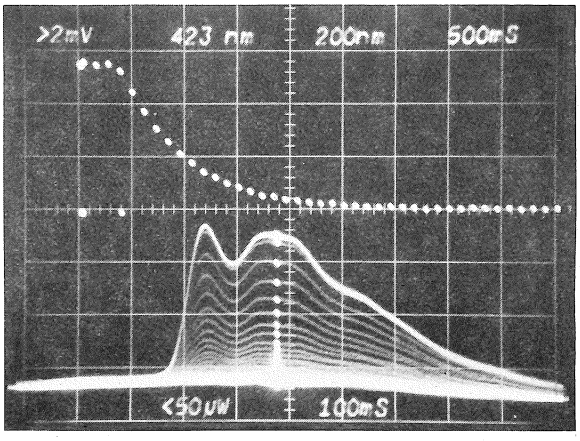


Fig. 3. Decay of phosphorescence from triphenylamine at 77 K is shown by curves. Lower group represents light intensity versus wavelength from about 330 to 530 nanometers, scanned every 100 milliseconds. Upper curve shows intensity at wavelength selected by marker spot (423 nanometers) versus time at 500 milliseconds per division. Decay constant of phosphorescence is 0.71 seconds. Both measurements were made and displayed simultaneously.

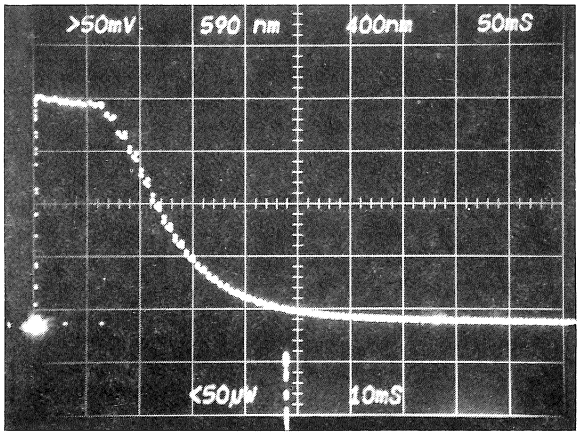


Fig. 5. Transmittance of bromphenol blue at 590 nanometers during reaction mentioned in Fig. 4. Zero per cent line is first graticule line and vertical sensitvity is 10 per cent division. Horizontal scale is 50 milliseconds per division. Curve shows that when flow started, transmittance leaped from 7 to 50 per cent. After flow stopped, transmittance dropped back to 7 per cent over next 250 milliseconds. Data shown are from five successive experiments superimposed upon one another.

intensity-wavelength data on the cathode ray tube of the oscilloscope. It is radiometrically calibrated, so that intensity can be read out in microwatts per nanometer. Readings can also be converted to transmittance or absorbance. Many of the advantages of modern oscilloscopes are provided, including readout of spectrometer settings on the display, compatibility with other plug-ins such as counters, amplifiers and time bases and triggering circuits for synchronizing the system with other units, including minicomputers.

The spectrometer is a compact Czerny-Turner, coma corrected, nonvignetting f/6 monochromator with two built-in interchangeable gratings. Depending upon which grating is used, either 40 or 400 nanometers of the spectrum are focused on the target of the camera tube. The precise region of the spectrum

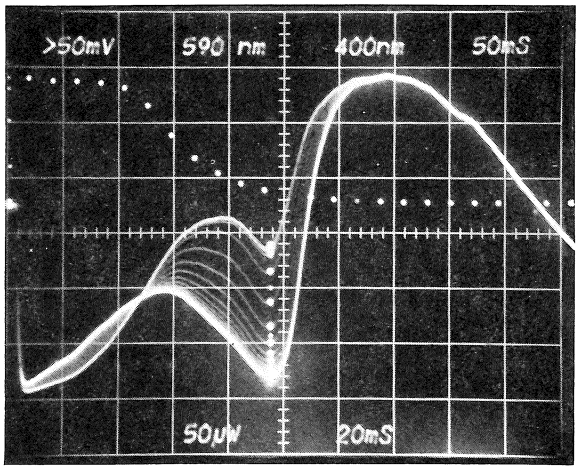


Fig. 4. Reaction of sodium bicarbonate and hydrochloric acid with bromphenol blue as indicator. Curves represent transmitted light intensity versus wavelength from 400 to 800 nanometers, scanned every 20 milliseconds. Dots show intensity at wavelength selected by marker spot (590 nanometers) versus time at 50 milliseconds per division.

observed can be varied by moving the gratings. The area of the vidicon target upon which the dispersed spectrum is focused is scanned by the electron beam in the vidicon. The voltage sweep that drives the vidicon beam originates in the oscilloscope plug-in and also drives the display beam in the oscilloscope cathode ray tube. As the spectrum dispersed on the vidicon target is read, the signal is amplified and corrected for system spectral response. The radiometrically corrected signal is then displayed on the CRT.

The vidicon is operated in two modes. One is the continuous scan mode at 4 to 20 milliseconds per scan for studying transient events. The other is the integrate mode in which the target is allowed to collect light for times up to one second or longer before scanning. This enhances the signal-to-noise ratio and increases the sensitivity of the system.

The wavelength of spectral features under observation can be measured with a marker spot, which is an intensified spot on the CRT trace. The marker can be moved to any part of the trace and the corresponding wavelength is indicated digitally on the face of the CRT. Furthermore, the radiometric intensity at the wavelength selected by the marker can be measured as a function of time if a second time base plug-in is used. Thus, the RSS can simultaneously give data out as intensity versus wavelength at selected time intervals and intensity versus time at a wavelength selected by the marker.

Wide range of uses

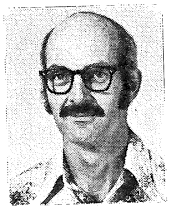
Applications for fast-scan spectrometers are as varied as the applications for which other spectrometers are now being used. Some strong application areas include photochromism, flash photolysis, flash lamps, explosions, flame emissions, atmospheric and solar monitoring, and monitoring of thin films during deposition. The following examples illustrate transient and steady-state events in production line and laboratory conditions.

Luminescent emission. When most organic molecules absorb light, they re-emit this light in the form of either a short-lived luminescence ($\sim 10^{-8}$ seconds) called fluorescence or a long-lived luminescence (seconds) called phosphorescence. Both of these emissions are useful in identifying and determining concentrations of organic molecules.

Fluorescence is widely used in biochemistry and pharmaceutical laboratories for chemical analysis. Phosphorescence, with equipment now existing, is a very complicated procedure and is not widely used at present. However, it remains the only and most sensitive method of determining many pharmaceutical molecules and air pollutants. The RSS has the potential to make phosphorescence analysis a convenient method of analysis (Fig. 3). The rapid-scan feature will allow an analyst to quickly choose optimum wavelengths of excitation and observation to perform an analysis of mixtures, something heretofore virtually impossible. Also as a result of the rapid-scan feature, an analyst can vary the delay time between excitation and observation, thus enhancing various phosphorescences of different decay times. This is called time-resolved spectroscopy. It is a technique used widely in neutron activation analysis (on a different time scale) but has never been commercially applied to optical spectra.

Absorption in a stopped-flow apparatus. Stopped-flow kinetics is a method of following the course of a chemical reaction optically. The usual procedure is to mix the reactants quickly (in milliseconds) by means of pneumatically operated syringes and a carefully designed mixing chamber. The mixed reactants are observed by passing monochromatized light through them and noting changes in transmittance by means of a photomultiplier. This technique follows the kinetics at a single wavelength, and the experiment must be repeated for every different wavelength desired. With the RSS, however, changes in transmittance over a broad wavelength can be determined in one experiment (Fig. 4 and 5). This greatly enhances the ability to observe intermediate steps in chemical reactions. Also, it will be possible to observe several simultaneous reactions active at many different wavelengths. In the future, analytical techniques using fast scanning may make possible simultaneous determination of many components in a single sample.

Monitoring of phosphors, light-emitting diodes, lamps and filters. The spectrometer in the RSS is radiometrically calibrated from 400 to 1000 nanometers. Consequently, absolute measurements of radiant power as a function of wavelength can be made. The information so provided can be used for comparing or sorting products such as phosphors (Fig. 6), lamps (Fig. 7) and light-emitting diodes (Fig. 8). Furthermore, the fast response of the instrument opens up the possibility of automated on-line examination and acceptance or rejection of LED's and other light-emitting, absorbing or reflecting components. □



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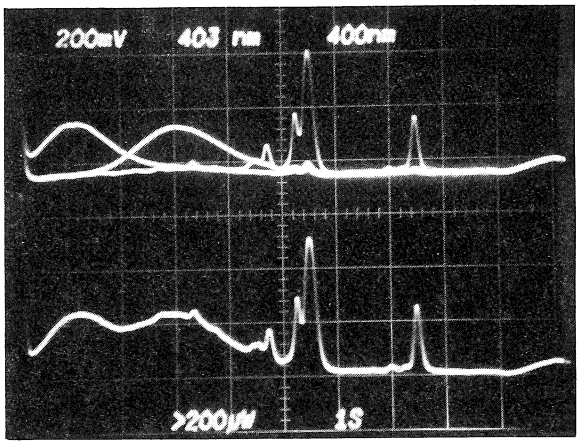

Fig. 6. Light emitted from blue, green and red phosphors in color TV set is shown in top curves. Each phosphor was excited separately. White light resulting from simultaneous excitation of all three phosphors is illustrated at bottom.

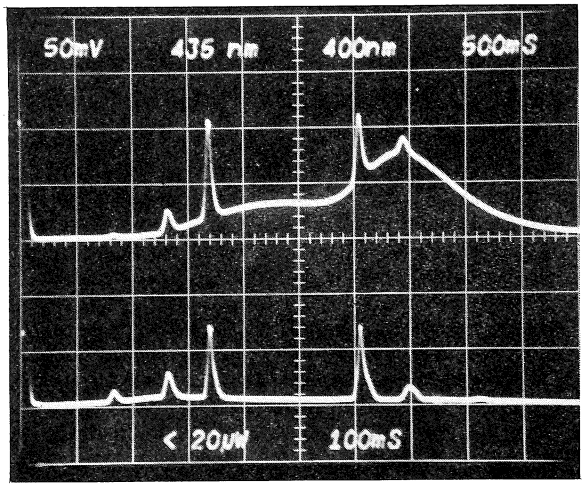

Fig. 7. White light emitted from fluorescent light bulb is indicated by top curve. Light emitted from mercury lamp (bottom curve) shows strong spectral lines, but little or no continuum emission.

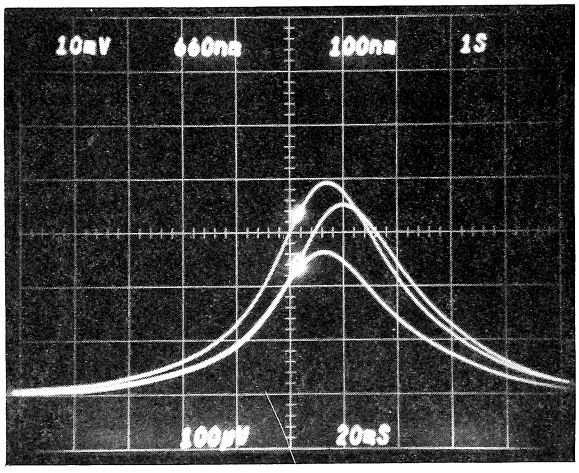

Fig. 8. Comparison of three different light-emitting diodes from same batch shows differences in peak intensity and peak wavelength over 610 to 710 nanometer range.