By Jere M. Marrs

Rapid-scanning spectrometry

MOLECULAR SPECTROSCOPIC AND CHEMICAL KINETIC APPLICATIONS

RAPID-SCANNING SPECTROMETRY has been with us for some time in various forms. The need for it arises when it is necessary to follow and record spectra that are evolving in time. The use of a vidicon tube in a rapid-scanning spectrometer appears to simplify the structure of such an instrument; the properties of the vidicon target offer unique advantages as a detector. The Tektronix J20/7J20 rapid-scanning spectrometer (RSS) is built around the vidicon system, and

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the description of that system and some of its chemical applications are the subjects of this paper.

Instrument description

Figure 1 shows a basic block diagram of the spectrometer system. The light to be detected passes through the entrance slit of a Czerny-Turner monochromator. Rather than an exit slit, the entrance slit is imaged on the plane face of a silicon vidicon tube. The resulting spectrum then is scanned horizontally off of the target by a 2-MHz, vertically rastered electron beam. The signal resulting from the scan then is displayed on

an oscilloscope screen, with light intensity measured vertically and wavelength horizontally. The time base used for the oscilloscope is also used for scanning the vidicon. The spectral information can be displayed either uncorrected for monochromator-vidicon response, or corrected such that the reading is radiometric. The correction circuitry is internal to the spectrometer, and is adjustable for calibration with a standard lamp. The J20/7J20 system is in two parts: the spectrometer, containing the monochromator, vidicon, and signal preamplification, and the electronic control unit, which acts as a plug-in to any Tektronix 7000-

Figure 1 *Basic block diagram of the rapid-scanning spectrometer system. The monochromator-vidicon section is shown in somewhat more detail.*
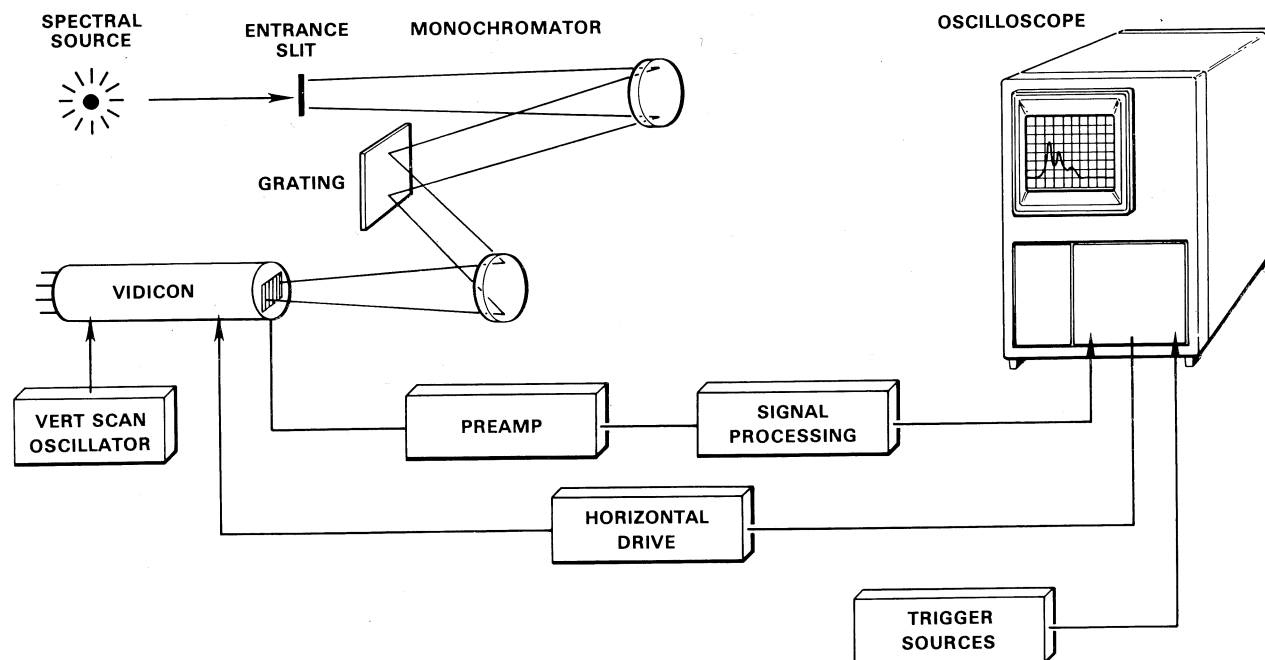
series oscilloscope. The spectrometer contains all adjustments to the monochromator, such as grating selection (two dispersions), slit width, filter selection, and displayed wavelength range. The electronic control unit allows one to select gain settings, scan times, and electronic display expansion, along with other controls associated with an oscilloscope. The important instrument settings, such as sensitivity, wavelength span, scan time, and the wavelength of a movable spot, are read out digitally on the oscilloscope screen. All of the instrument features and performance ranges, if discussed exhaustively, would be quite lengthy, and so perhaps it would be best merely to summarize its function. A spectral range of as little as 4 nm and as much as 400 nm may be displayed with calibrated scan speeds as fast as 40 nm/msec. The sensitive range is 300 to 1100 nm, using the silicon vidicon. The sensitivity and dynamic range are determined by the vidicon and the manner in which it is used. This will be discussed later.

The spectrometer can be used for recording either luminescence or absorption spectra. In the absorption mode, one can display either %T or absorbance by the appropriate vertical gain selection. Luminescence spectra can be recorded uncorrected for spectral response, or with the internal radiometric calibration.

Detector

The silicon vidicon offers some interesting advantages as a detector for a rapid-scanning spectrometer. Since the entire spectrum to be scanned is imaged on the vidicon and is scanned by an electron beam, there are no moving parts to effect the scanning. The problems associated with mechanical inertia are eliminated, and the

problems of nonreproducible baselines, brought about by multiple mirror reflectance mismatch and differential aging, are eliminated. The signals from the vidicon can be subjected to signal averaging. The vidicon target has the property of storing light intensity signals until they are "scanned off" by the electron beam. One can thus delay scanning for a time, allowing the vidicon to act much like a photographic plate, and then scan the information from the target quickly. This procedure is used in the "integrate mode" of the spectrometer, greatly enhancing its sensitivity to weak spectral sources. Such a mode of operation uses the multiplex advantage of the vidicon. The detector target receives and stores spectral information at all wavelengths of the chosen 40- or 400-nm span at all times. It is then read out by the electron beam. A detector such as an image dissector, or rapid-scanning by means of rotating mirrors or gratings, does not have the multiplex advantage since information is obtained at only one wavelength at a given time. Therefore, the vidicon seems uniquely suited as a detector for rapid-scanning spectrometry. The ability of the vidicon to follow optical signals varying in time is a function of the absolute intensity of the light and the scan rate of the vidicon. For the extreme case of Signal on:Signal off, for an intense source, the useful time resolution is about 10 msec at a scan rate of 40 nm/msec. For the case of a strong light source that changes only a small amount, the ability of the vidicon to follow the change is considerably enhanced. With the storage property of the target, it is possible to record spectral events occurring on a time scale that is short with respect even to the fastest scan time. The time evolution of the spectrum could not be followed, say, for a

picosecond flash, but no spectral information would be lost. The dynamic range of the vidicon is determined by the scan rate and the integrate time. The faster the scanning, the greater the dynamic range yielding a desirable trade-off between sensitivity and dynamic range.

Applications

Applications for the rapid-scan spectrometer include both absorption and emission studies. In most cases the time-resolution aspect is the important one, but the simple convenience of being able to see a large spectral region, essentially continuously, has some advantages in systems that do not evolve in time, or change slowly.

One most interesting application of the RSS is in molecular luminescence.[1] When molecules are excited with light, they may relax to the ground state by emitting radiation in the form of fluorescence (short-lived), phosphorescence (long-lived), or both. The study of molecular luminescence has value in investigating molecular structure and chemical properties of molecules as well as in quantitative analysis. The RSS offers some advantages to both of these fields.

The molecular electronic spectroscopist looks at the fluorescence and phosphorescence of molecules and chemical systems as a probe into the structure of the molecules and the chemical interactions between molecules. The photochemist uses molecular luminescence to follow the paths for relaxation of electronically excited molecules in order to gain knowledge about photochemical reactions. The properties of molecular luminescence of interest to the spectroscopist and photochemist are: emission band spectral location, shape, vibrational structure, intensity, polarization,

and lifetime of decay. The RSS can give all of this information very quickly, and in the case of lifetimes has an advantage over other methods. The RSS has calibrated scan times as fast as 10 msec, and therefore can be used to follow phosphorescent decay while displaying the entire spectrum. The slower scan times can be used for the longer decays. If one is doing a phosphorescence experiment with a mixture of phosphorescing molecules, the RSS can *time-resolve* spectra of individual molecules by taking advantage of their differing lifetimes. A molecule with a long phosphorescence decay lifetime (exponential decay) usually has a comparable risetime during excitation. Thus, by adjusting the duration of excitation and the time interval between excitation shutoff and observation, one can enhance the observation of either the long- or short-lived molecular phosphorescence. The intensity of the two spectra can be observed simultaneously while adjusting these parameters. Thus routine phosphorimetric analysis of mixtures could become a convenient and viable method.

The RSS also can be used to monitor a molecular luminescence while changing temperature or excitation spectral region, or during the addition of chemical perturbations. Considerable time and effort can be saved in performing these experiments as compared to that of other methods.

By placing a sample between a light source and the RSS, one can obtain the absorption spectrum of the sample. By use of the external correction circuitry, the display of a smooth, continuous light source can be adjusted to a straight line on the CRT of the oscilloscope. Any absorption thus would have an origin from a flat baseline. The quantity read linearly on the CRT in that case would be percent
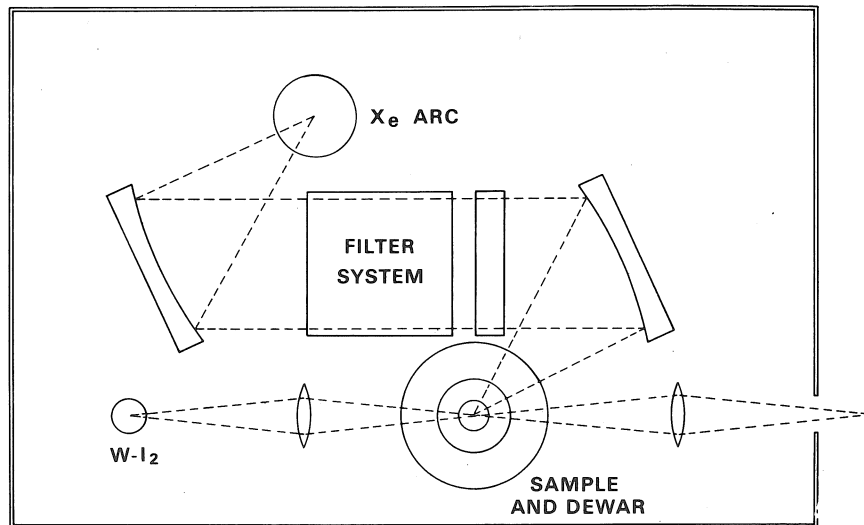

Figure 2 *Experimental apparatus used to examine low-temperature molecular luminescence and triplet-triplet absorption.*

transmission. Once the 0% and the 100% lines have been established, one can expand the scale by increasing the vertical sensitivity of the RSS. With a standard of transmission, the "window of %*T*" can be established.

An interesting experiment was performed in our laboratory in which triplet-triplet absorption was observed. An experimental apparatus (such as that shown in *Figure 2*) was constructed, which allows one to observe the absorption of a sample while irradiating it with ultraviolet light from a dc xenon arc. The sample consisted of a solution of diphenylamine ($\sim 10^{-4}$ M) in EPA (a mixture of diethyl ether, isopentane, and ethyl alcohol) frozen in a quartz sample tube to a clear, rigid glass at liquid nitrogen temperature. When the ultraviolet irradiation was turned on (via a shutter), an absorption developed with a maximum around 550 nm. When the irradiation was shut off, the absorption decayed with the same rate constant as the phosphorescence emission of diphenylamine. This showed that the absorption had its origin in the triplet (phos-

phorescent) state of diphenylamine. This T-T absorption was reported in the literature in 1967 by Henry and Kasha.[2] This irradiation-induced absorption is called *photo*chromism, and the RSS is ideal for studying it. Similar experiments could be performed illustrating *thermo*chromism, which is temperature-induced absorption.

The RSS is most useful when observing spectra that evolve in time. A very exciting application is stopped-flow kinetics. The information one gains about a reaction while observing the entire spectrum (or 400 nm of it) is powerful indeed. Chemical kinetics, when followed spectrophotometrically, is subject to several pitfalls. The usual approach is to monitor the transmission of the reaction at a fixed wavelength as a function of time. Such measurements, while quite precise, often will give erroneous information if spectral peaks shift or if there are transient absorptions during the reaction. If one could observe a rather large spectral region during the reaction, all of the kinetic data could be extracted while observing
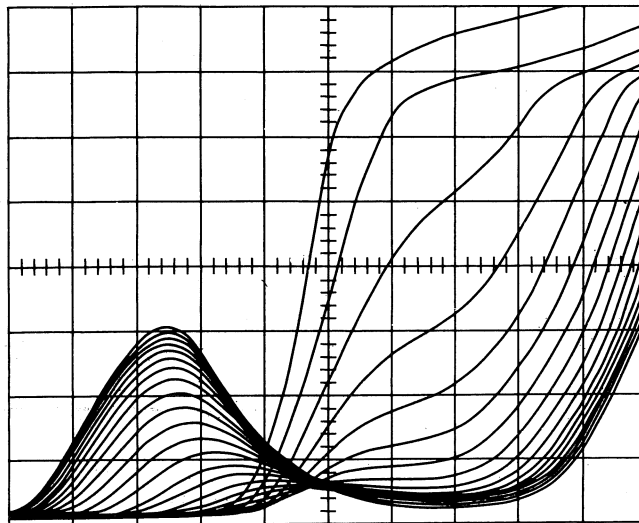
Figure 3 *A drawing of actual CRT data showing the reaction of USP formaldehyde solution with aqueous acid dichromate. Wavelength span is 200 nm (470–670 nm). Scan time is 200 msec.*

any spectral shifts or intermediate absorptions that could interfere with the measurement. The RSS allows one to observe a 400-nm spectral range in one scan (of 10 to 200 msec duration), making it ideally suited for the stopped-flow kinetic scheme.

In stopped-flow studies, the reactants are mixed together and pumped into the optical absorption path in just a few milliseconds. The absorption is then followed during the reaction. The type of information one gets in this experiment is illustrated in *Figure 3*. This is a relatively slow reaction ($\sim$2 sec) in which USP formaldehyde solution is oxidized with dichromate. The depletion of the dichromate can be followed on the right-hand side of the spectrum ($\% T$ increases vertically) while the build-up of the chromium (III) ion can be seen on the left. It is interesting that the dichromate disappears much faster than the Cr^{3+} builds up, and that the absorption trough shifts in wavelength during the build-up. The reaction evidently is quite complex, and this is just the sort

of information that one can get with the RSS. Ligand-exchange reactions have been studied using this basic technique, and intermediates have been observed, allowing an accurate mechanism to be determined.[3]

The preceding examples provide some idea of the applications possible with the RSS. There are, of course, many more specialized uses, such as flame emission, arc emission, plasma emission, and others. The built-in radiometric calibration allows its use in non-chemical applications also. The utility of the RSS appears to be quite diverse.

References

1. MARRS, J. M., Paper 48, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio (1972).

2. HENRY, B. R. and KASHA, M., *J. Chem. Phys. 47*, 3319 (1967).

3. SANTINI, R. E., MILANO, M. J., PARDUE, H. L., and MARGERUM, D. W., Paper 227, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio (1972).