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Hewlett-Packard's philosophy of product development, particularly in entering a new field of interest, requires that a new product make a real contribution to its field. It must fill a need rather than simply offer another brand of something already available.

As the company's communication channel for "technical information from the laboratories of Hewlett-Packard," we get to report on most of these contributions. As a result, we're used to seeing innovations—in fact, we expect them.

Once in a while, however, a product comes along that is so different and so innovative that it deserves to be called revolutionary. Usually it's the result of a creative inspiration transformed by engineering talent into a useful product that does a particular job better by far than anything that's come before it.

The 8450A Spectrophotometer is this kind of product. Quite simply, it does things that other spectrophotometers can't. It makes it practical to do measurements and analyses that were seldom or never done before because the effort was too great. And it does the ordinary things that spectrophotometers do, but it does them faster and more accurately.

Just what do spectrophotometers do? By measuring the light absorbed by a sample consisting of a known compound dissolved in a solvent, they can find the concentration of that compound in the sample. By measuring how much light of different wavelengths an unknown sample absorbs, they can gain information about what's in the sample. (The hand in the cover photo is holding a typical sample cell containing a red dye.) Spectrophotometers are widely used in biochemistry and in organic, inorganic, and analytical chemistry.

The creative idea that led to the 8450A Spectrophotometer was simultaneous detection of all wavelengths matched with a powerful processing capability. While traditional instruments start out by filtering the light so that measurements are made one wavelength at a time, the 8450A sends all wavelengths through the sample at once, then separates them afterwards and measures them all simultaneously. Naturally this makes things go much faster. But to turn that creative idea into a viable product, several key technical difficulties had to be overcome.

Most of the articles in this issue deal with what was done to solve those problems. Then on page 31, Dick Monnier attempts to relate what the other articles can't—the ups and downs, the technological milestones, and especially the people of a project like this.

-R.P. Dolan

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Design and Performance of a Highly Integrated Parallel Access Spectrophotometer

This innovative ultraviolet/visible spectrophotometer solves many chemical analysis problems that were impossible for older photometric technology.

by Barry G. Willis

ULTRAVIOLET/VISIBLE SPECTROPHOTOMETRY is a chemical analysis technique used for nondestructive analysis of a wide range of molecules and compounds. Examples extend from simple inorganic metals and nonmetals, such as those found in dopant or plating processes, to complex organic and biochemical species. Samples are analyzed rapidly, reproducibly, and accurately. The technique can be used to determine both the type of a compound and its concentration, often to very low detection limits. Depending on the electronic structure of the compound, the limit of detectability can be in the range of 1×10^{-8} mole/liter or better (approximately one part in 10^9, depending on molecular weight). More important, analysis of everyday concentration levels can be done with precision and high productivity.

For species of biochemical interest, UV/Vis is often the method of choice. Compounds with very large molecular weight can be analyzed with extreme specificity in the complex mixtures found in biological fluids. For example, enzymatic reactions, in which the compound of interest is a catalyst for other materials, are important for diagnosis of a variety of life-threatening disease states. As a result, enzymes are analyzed over a million times each day for clinical purposes. In physical measurement situations, UV/Vis is used to monitor the thickness and uniformity of coatings, color perception, reflectivity, particle density and size distribution, and surface interactions of materials.

UV/Vis spectrophotometry analyzes the absorption of light by a sample, typically in the wavelength range from 200 nanometers (nm) to 800 nm. The major features are the wavelength of the absorption, which gives molecular information, and the degree of absorption, which gives concentration information.

UV/Vis has wide applicability because it is sensitive to the basic electronic transitions of the molecules involved. However, since the electronic molecular orbital transitions in solution are broadened by vibrational, rotational, and translational interactions, absorption bands in this region of the electromagnetic spectrum tend to be relatively large compared to most qualitative analysis techniques. Traditionally, this broadness has limited qualitative analysis by UV/Vis to identification of specific functional groups or chromophores (the portion of a molecule that has a strong electronic transition). Conversely, it has been this broad-

ness and high interaction probability of the electronic structure of the molecules that gives the technique its great advantage in quantitation of chemical species. In other words, UV/Vis isn't the best way to find out what's in an unknown mixture, but if you know what's there, UV/Vis will tell you very accurately how much.

The traditional approach to the measurement, illustrated in Fig. 1, consists of a wideband source, a monochromator to select the wavelength of interest, a dual-beam ratio system, and the detector. Typically, if qualitative information is needed, the monochromator is scanned over the region of interest and the measured data is output to a recorder. For quantitative purposes, the monochromator would typically be held at a single wavelength (that of maximum sensitivity and independence from interference) and the response would be compared to a previously standardized result.

As chemical needs have grown more complex and demanding, the technological capability of UV/Vis has not kept pace. An example of this is baseline flatness, which is the degree of deviation from an average value as a function of wavelength. In a traditional system baseline flatness depends on the quality of match between the optical components in the sample and reference paths. This also requires that the optical cells that contain the sample be matched. Matched cells can be obtained, but it is difficult to maintain them in a state of equal cleanness. In some spectrophotometers it is possible to scan the system and normalize a limited mismatch over fixed intervals. This takes a sig-
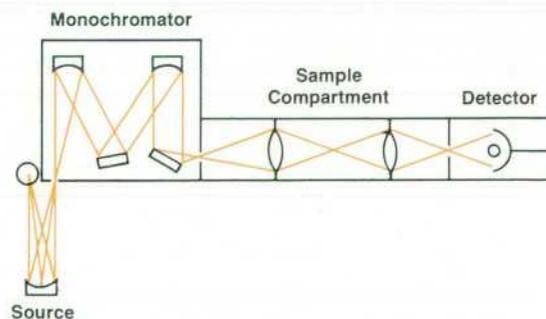
Fig. 1. *In a traditional spectrophotometer, a monochromator selects one wavelength of light at a time to pass through the sample to the detector.*

Fig. 2. *Model 8450A UV/Visible Spectrophotometer is designed to overcome many of the limitations of traditional spectrophotometers and provide chemical information that formerly had to be ignored. A high degree of integration between its processor, optics, and keyboard helps maximize its speed, accuracy, sensitivity, and productivity.*

nificant amount of time, however, and if any spectral shifts occur between normalization and the measurement, the resultant baseline drift makes accurate absorbance measurements near the baseline very difficult and time-consuming. A practical result is that system normalization over more than a single wavelength is not feasible. Hence baseline flatness limits precision near the detection limit.

The wavelength dispersing mechanism in a traditional monochromator is a series of mechanical linkages that rotate a grating (the most common device for separating light into its component wavelengths) to the necessary angle. Irreproducibility in the linkage means uncertainty in the actual wavelength selected. One consequence is errors in the measurement of absorption data that changes with wavelength. This means that for precision measurements all quantitation must be done in low-slope regions (peaks and valleys) of the absorption curve.

These are examples of a couple of photometric measurement limitations that are imposed by the instrumentation available. Others include structurally imposed problems, limitations on sample exposure because of detector configuration, fluorescence sensitivity and concomitant error in absorbance at the wavelength of interest, resolution variability causing uncertainty in absolute absorbance, and stability problems imposed by a variety of structural limitations and variable detector gain (the most common detector has a certain amount of hysteresis).

These limitations have long been imbedded in the technology available. As a result, procedural adjustments and chemical modifications have been adopted to avoid or overcome them. One of the most serious procedural changes has been that, in today's demanding chemical environment, where more and more complex mixtures need analysis to lower and lower limits, photometric measure-

ments have not been able to solve the problems uniquely. This has caused a shift to more time-consuming, less precise, and chemically destructive techniques. The conventional wisdom is that UV/Vis does not have the necessary sensitivity or ability to handle even relatively simple chemical mixture problems.

New UV/Vis Spectrophotometer

In designing the HP 8450A Spectrophotometer, Fig. 2, we decided to address ourselves directly to bringing high performance and technical excellence to the measurement

Absorbance Units

Model 8450A Spectrophotometer computes the absorbance of a sample according to the equation

$$A = -\log_{10} \frac{S-D}{R-D} - B$$

where S and R are measurements of the light reaching the detector via the sample and reference paths, respectively, and D and B are corrections for dark current and the degree of balance between the two paths. Absorbance is measured in absorbance units, or A.U. (The abbreviation Abs for absorbance units is sometimes used, and sometimes "absorbance units" is abbreviated to "absorbance"—e.g. 3 absorbance or 3 Abs for 3 A.U.)

Beer's Law states that the absorbance A of a substance is related to its concentration C by:

$$A = abC$$

where a is the molar absorptivity (or simply the absorptivity) of the substance and b is the sample path length.
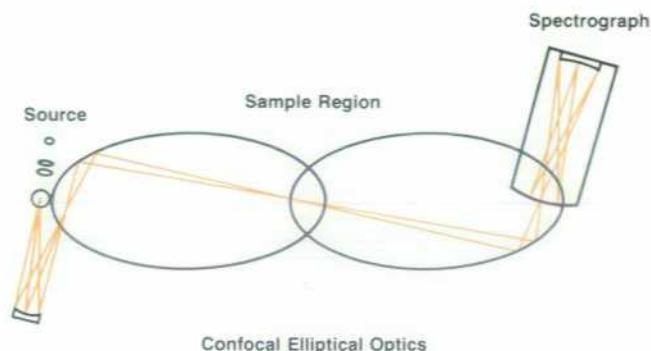
Fig. 3. *In the 8450A, traditional optics are reversed. The light passing through the sample is wideband instead of a single wavelength. The detector is a spectrograph that measures all wavelengths simultaneously instead of one at a time.*

process. Taking advantage of the capabilities inherent in the design, we have expanded the range of applicability of spectrophotometry to include chemical information that had to be ignored in more traditional approaches.

The design process focused on maximizing speed, accuracy, and sensitivity to provide a highly productive instrument. The 8450A represents an extraordinary match between the capabilities of processor, optics, and keyboard control system. For the first time, a photometric measurement system is fast enough to allow direct interaction between the user and the chemical or physical measurement task being performed. That is, interactive adjustments can now be made on the basis of immediately obtainable chemical information. Also, chemical measurements can be made that were previously impossible or impractical because of the precision required or the time involved.

Reversed Optics

The basic concept is to turn the measurement arrangement around, as shown in Fig. 3. Now the sequence is reversed compared to the more traditional design approach shown in Fig. 1. The source is now focused on the sample instead of the monochomator. After passing through the sample, the remaining light enters a spectrograph, rather than a monochromator. This allows access to all the wavelength information simultaneously, rather than serially as with a monochromatic system. Now, instead of having to acquire data at a rate of one time constant per resolution element, we can acquire the same information on all resolution elements simultaneously. This means that we have a fundamental speed advantage related to the number of resolution elements involved. In this case, it is a factor of four hundred. Being four hundred times as fast as a traditional system is not the whole name of the game, however. Even more important is that we now have direct, rapid electronic access to wavelength information. Also, since there are no moving parts in the spectrograph, the uncertainty caused by wavelength irreproducibility is avoided. Now valid quantitative chemical information can be retrieved from the sides of absorption peaks as well as the tops. This additional information makes chemical species more unique and makes identification more of a possibility for UV/Vis.

Baseline stability in a reversed optical system can be a

Analysis for Metals

by Gerald E. James

Quantitation of metals in solutions containing several metals is of interest in a variety of industries including metal plating, semiconductors, mining, steel, and others. In the past it has been necessary either to separate the metals before spectrophotometric analysis or to use chemical procedures to generate a chromophore specific for each metal of interest in turn. The 8450A offers the potential of eliminating much of this premeasurement manipulation by means of the multicomponent analysis routine.

For example, many metals exhibit spectra in the ultraviolet region when in strong hydrochloric acid, but the usefulness of this has been limited because of the mutual interference of the spectra when several metals are present simultaneously.
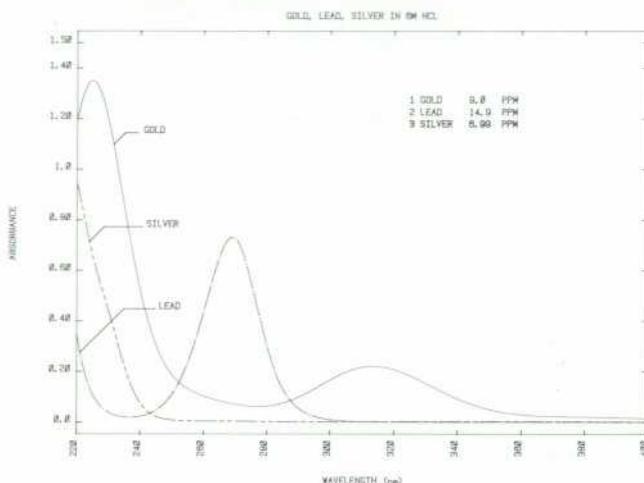
Fig. 1. *Spectra of gold, lead, and silver in strong hydrochloric acid.*

Fig. 1 shows the spectra of gold, lead, and silver in 6M HCl at about 10 ppm each. Fig. 2 shows the first derivatives of the same spectra and the results for analysis of two different mixtures of the three metals. The derivative spectra were used to take advantage of their amplification of spectral detail and immunity to changes in baseline signal level. The results are excellent and the concentrations of 1-15 ppm are well within the sensitivity limits for the 8450A.
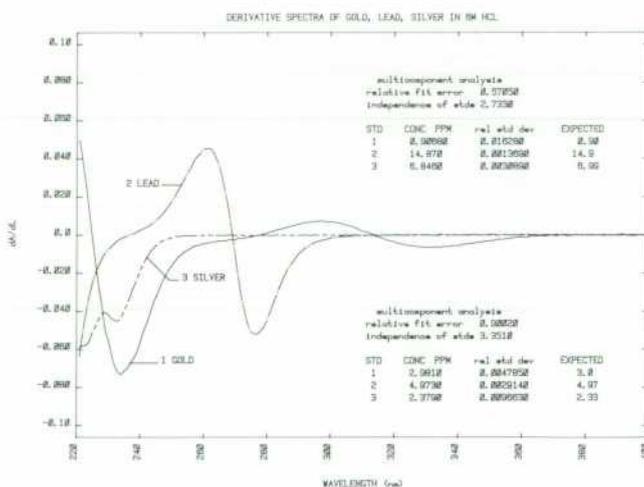
Fig. 2. *First derivatives of the spectra of Fig. 1.*

serious problem. Since the sample cell is ahead of the spectrograph entrance slit, any optical variations induced by the sample cell look like absorption of light. The slit is 50 micrometres (μm) wide. If the desired photometric accuracy is one part in ten thousand, movement of any image shadows must be kept to less than 0.5 μm at the slit. For practical purposes, this means that even if the entire optical system is fixed, including the necessary flow cell, thermal variations in the structure would add sufficient expansion and contraction to limit the accuracy of the results. A standard replaceable cell cannot be used, since the cell cannot be replaced with sufficient accuracy. This places a tight restraint on the utility of such a system.

Clearly, to take care of the optical variability of cell replacement, an adaptive optical system is required. The new 8450A Spectrophotometer has just such a system. The beam director system (see article, page 24) senses the position of the beam after it goes through the sample cell and compensates the image position with a reproducibility better than three seconds of arc. That is better than the angle subtended by a lateral displacement of less than 1.5 cm in a kilometer (less than an inch in a mile). With an active optical element in the system, high-quality measurements can be made even in the presence of variations of the index of refraction as air currents pass through the sample area.

Since the source intensity is variable in both wavelength and time, some technique must be used to normalize the source output. Traditionally, this is accomplished by a dual-beam approach, with the light passed alternately through a reference cell and the sample cell. These repeated readings of source intensity, concurrently with any variations induced by reference solution instability, help to normalize the intensity read at the sample cell. This dual-beam approach improves spectral stability to the limits imposed by detector nonlinearity and amplifier offset. Even so, restrictions in the optical arrangement usually used by designers constrain the system to a single reference and a single sample cell position. The 8450A beam director system is radially symmetric and can accommodate as many beam positions as space allows, which turns out to be one reference position and four sample cell positions.

Elliptical Optics

This brings us to the basic optical design. The sensitivity of photometric measurements is usually limited by the statistics of beam balance uncertainty (the uncertainty of the match between the sample and reference paths), and if not by that, then by the shot noise of the photon flux available. The new HP system has excellent beam balance charcteristics, so the actual low-level absorbance limit is tied to the amount of light that can be pushed through the optical system. Traditional spherical optical design would have left us with a system not much better than existing ones, so a radical departure was made. Elliptical optics have better light-gathering characteristics but have been difficult to make because of the difficulty of grinding a surface that lacks spherical symmetry. Using numerically controlled machining techniques guided accurately by an HP laser interferometer, an elliptical bowl was ground in pyrex. This became the master surface from which the first 8450A's mirrors were made. Current 8450A mirrors are made using a master surface that was ground using more conventional

techniques. However, this first master proved the feasibility of grinding the elliptical surface.

The folded optical system is described in the article on page 17 and illustrated in Fig. 1 on page 17. As many as five beams can be accommodated. The lamphouse, spectrograph, and beam director assemblies are close to one another and mounted on the same plane. This means that the system is more independent of thermal effects than those traditionally designed on an optical rail concept and physically spread out. Since these components are on the same plane, construction and adjustment of the system during manufacture is also simplified.

Chemical Identification

by Gerald E. James

It is frequently of interest to identify a component when it could be any one of several having very similar absorption spectra. The capabilities of the 8450A were demonstrated by using it to identify which of four barbiturates were contained in some test solutions. In practice, a barbiturate spectrum is measured as the difference between two spectra measured at pH>13 and pH=10.3. This is done to cancel the absorbance of components that do not exhibit a spectral shift with pH, which would otherwise interfere. Fig. 1 shows the difference spectra for four important barbiturates. The spectra are extremely similar, differing by 2 nm or less in their absorbance maxima and minima. However, if great care is taken in making dilutions of the standards and samples and in not introducing noninstrumental measurement errors, it is possible to ascertain which of the barbiturates is present in an unknown and to compute its concentration. Several alternatives are available for identification, such as the 8450A multicomponent analysis routine or division of the spectrum of the unknown by that of each standard. The relative-fit error statistic obtained from the multicomponent analysis is an excellent indicator of spectral match. If the spectra are of the same compound the division of one spectrum by another should produce a quotient that is a straight line when plotted versus wavelength. Such spectral comparisons are made possible by virtue of the excellent wavelength reproducibility of the 8450A.
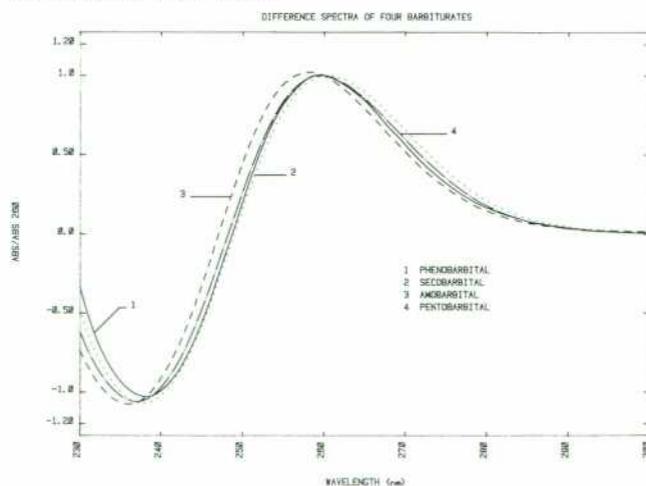
Fig. 1. *Barbiturate spectra are measured as differences between two spectra measured at pH>13 and pH = 10.3. These four barbiturates have very similar spectra, yet the 8450A can distinguish them.*

The spectrograph uses a pair of integrated photodiode arrays designed and built by HP Laboratories. These are special high-stability, low-noise, high-accuracy arrays with 211 detectors on each chip.

Since the system moves the beam director and gets it settled accurately three times a second, reads the leakage current on each diode, levels the gain on each to maximize measurement range and precision, reads the reference and sample beams twice and calculates all necessary corrections, a large amount of mathematical manipulation is necessary. This is handled by the MC5 silicon-on-sapphire microcontroller chip produced by HP. It can handle high-speed calculations and the large amount of I/O communications required to control an instrument such as this. The SOS technology carries with it added reliability, which is important for instrumentation in the chemical field.

Control and Communications

Fig. 4 shows a block diagram of the overall control and communications system. A spectrophotometer with the 8450A's capability and high level of performance integration would simply not work without the microprocessor as an integral part of the design. All modern chemical instrumentation includes microprocessor control of some sort, but the difference here is one of integration and taking advantage of internal control characteristics of the processor rather than simply adding a processor to existing technology. The interactive control program occupies 57,344 bytes of read-only memory (ROM). It was especially designed to make control of the instrument highly user-oriented instead of instrument-oriented, and to preserve a highly interactive approach.

Keeping track of the volume of data generated during the optical measurement process can be formidable. In the 8450A, however, the system is as transparent as possible so the user need not even be aware of the processing involved. Besides the ROM control memory, the processor makes use of 32K bytes of random-access read-write memory (RAM). This is expandable to 64K bytes. To supplement the high-
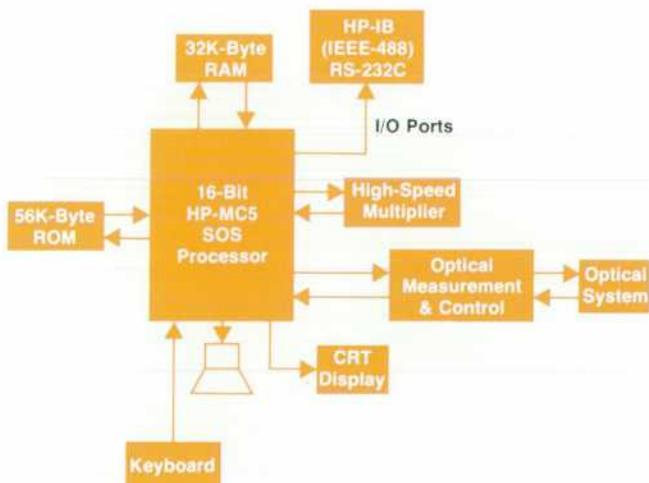
Fig. 4. *Model 8450A Spectrophotometer is controlled by a microprocessor. The control program, which occupies 56K bytes of read-only memory, is highly interactive and user-oriented.*

Pharmaceutical Formulations Analysis

by Gerald E. James

In the pharmaceutical industry government regulations require quality control testing for the active ingredients in the products. These ingredients absorb ultraviolet and occasionally visible radiation. However, because of mutual interference by components, multi-ingredient formulations have required separation of components before spectrophotometric analysis, or chemical treatment to permit sequential measurement for each component. The multicomponent analysis capability of the 8450A is ideally suited to formulations testing in that no separation or chemical treatment to eliminate mutual interference is necessary. One simply uses as standards the spectra measured for known concentrations of the individual components and then measures the spectrum of the product. The same solvent is used to dissolve the standards and the product. The measurements require one second each and the computations usually five to ten seconds. The 8450A computes the proportions of the standard spectra that when added together best match the spectrum measured for the mixture. An example of this is the analysis of a headache tablet for its active ingredients acetominophen, caffeine, salicylamide and aspirin (salicylic acid). Fig. 1 shows the spectra for the individual components, the spectrum for the tablet formulation and the printout of results.

Since the multicomponent analysis computation can be done repetitively at specified time intervals the 8450A offers great potential for routine testing of multi-ingredient tablet dissolution rates.
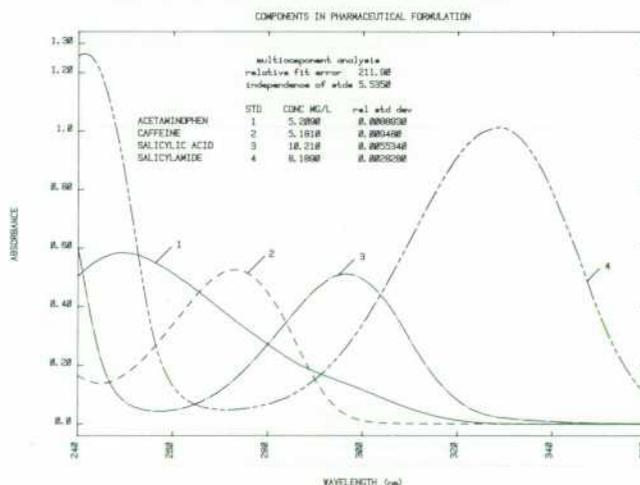
Fig. 1. *Results of an 8450A multicomponent analysis of a headache tablet. The analysis was done without separating the components first. The standard deviations of the measured concentrations indicate the degree of uncertainty in the measurements.*

speed computation capabilities of the MC5 processor, we have added a hardware multiplier to the system. The processor can send it a pair of numbers to be multiplied, do some interim calculations in parallel if necessary, and be ready for the result from the multiplier when it is completed. The system does over 200,000 distinct operations to output the absorbance data.

The optical system is under direct feedback control of the

Liquid Chromatographic
Determination of Steroids

by Barry G. Willis

The compounds shown in Fig. 1 are very similar spectrally. One can see that cortisone and dexamethasone have very nearly the same peak positions, differing only by the shoulder in the 260 to 270 nm region in dexamethasone. Corticosterone is shifted only 4 nm to the longer wavelengths, but has a peak shape very similar to cortisone's. By the traditional approach to spectrophotometry, these three compounds could not be analyzed in a mixture and would have to be separated somehow before analysis.
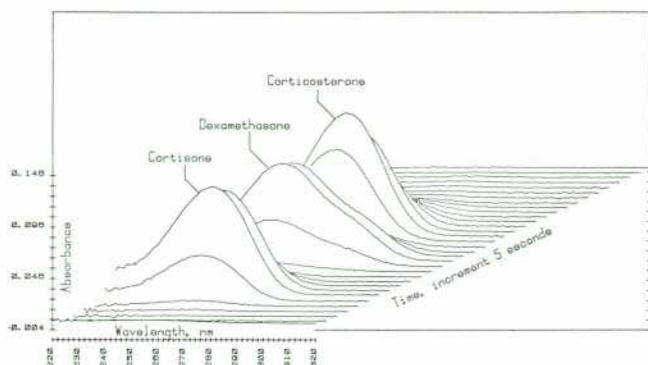
Fig. 1. *Pseudo-isometric presentation of the liquid chromatographic separation of the three steriods, cortisone, dexamethasone, and corticosterone, all at 300 ng/µl. The HP 1084A Liquid Chromatograph system was used with the 8450A Spectrophotometer as a detector. The HP 9825A Desktop Computer controlled the plotter to produce this plot.*

High-pressure liquid chromatographic separation is currently the method of choice for this mixture, both for the simplicity of the procedure and the sensitivity of the technique. Since the compounds are so similar chemically, bulk separation and analysis is both tedious and inaccurate because of variable recovery levels. A single-wavelength detector could be used, such as those using the mercury 254-nm emission line source. Since the compounds all absorb and there is a good signal from that source, reasonable sensitivity can be attained. With a variable-wavelength detector, such as that available on the HP 1084A Liquid Chromatograph, greater sensitivity can be attained by moving closer to the peak maxima in the region about 234 to 238 nm. By using the HP 8450A as a detector, not only can spectral information be obtained, thereby improving the qualitative nature of the analysis as shown in Fig. 1, but quantitative characterization of the mixture is enhanced by the use of more of the chemical information than was previously available.

There's more to the story than that, however. We find that the multicomponent capability allows spectral isolation of species without
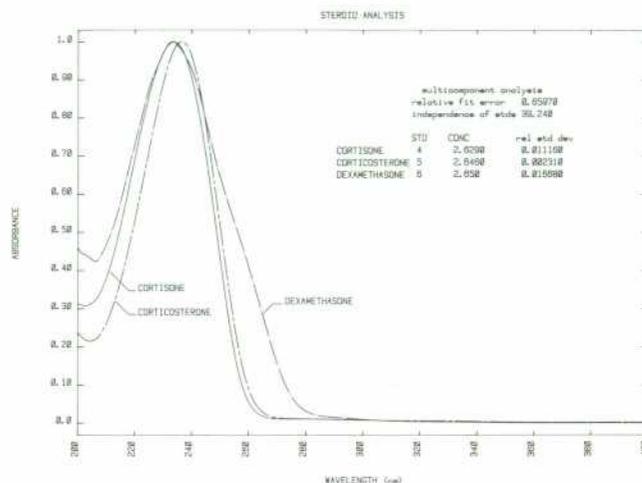
Fig. 2. *Spectral plots of each of the steriods at eight parts per million. Each is normalized to a peak value of one to emphasize the spectral similarity. The actual absorbance values are close to one. In the upper right is a printout of a direct 8450A analysis of the steroids in the mixture, done without separation at 2.667 parts per million.*

separation in a wide range of routine situations. Fig. 2 shows the standard normalized spectra of the three steroids at a concentration of eight nanograms per microliter. A mixture containing 2.667 nanograms per microliter of each of the compounds gives a composite spectrum roughly the same magnitude. The resultant spectral multicomponent analysis should give a value of 2.667 ng/µl for each. The actual values obtained are printed by the spectrophotometer in the upper right-hand corner of Fig. 2. The errors, using the derivative with respect to wavelength, were 1.4%, 0.8%, and 0.6% for cortisone, dexamethasone, and corticosterone, respectively. With this level of accuracy, one can infer that the limit of analysis is in the region of 20 picograms per microliter, or 20 parts per billion of one of the components, such as cortisone, in the presence of the other two at the original level of 2.667 parts per million.

Being able to analyze a simple mixture such as this directly affords a significant enhancement in analysis speed and productivity of the laboratory involved. However, in very complex mixtures, or systems without even minor spectral orthogonality, LC separation prior to full spectral analysis can greatly facilitate rationalization of difficult chemical systems. Because of the multibeam configuration of the 8450A, a flow-cell sample position can be maintained for LC analysis, and the other three sample positions can be used in a multiplex manner for general-purpose analysis of simpler situations.

processor. The processor minimizes the exposure of the sample, using only as much as necessary. This is important with photosensitive samples. In a one-second measurement the total sample exposure is about 200 milliseconds, depending on the exact speed of the beam director. Thus the total integrated flux on the sample is very small. We have repetitively measured photoresist compounds for long periods of time with no measurable degradation to the limit

of the statistics of the system, which is in the 10^{-4} absorbance-unit range.

The input gain circuitry is also under processor control. As the output of each detector diode is read out to the analog-to-digital converter, the system sets up for maximum precision by adjusting the input gain to a value that is optimum for that diode.

Interactive User Interface

To make it useful in a wide range of applications, a system must have an efficient, natural, and interactive user interface that helps the user get the desired results quickly and easily. This is true whether the measurements to be performed are general tasks of quality control that are repetitive in nature or esoteric manipulations of data to gain understanding of a research problem.

The 8450A's dedicated keyboard is oriented toward the types of measurement tasks to be performed. Keyboard commands have sentence structure, with a subject, verb, and object. The EXECUTE key serves as the period of the sentence. Often the source or destination of information is implicit, so the 8450A doesn't always require an explicit statement of the operations to be done. Also, since many operations are repetitive, the user isn't required to repeat inputs that don't change.

The main portion of the control system has been kept as simple as possible for the casual user, and operations of a more sophisticated nature remain in the background with a number of default conditions. The user who wants to change the default conditions certainly can do so, but additional background to program those changes with knowledge of their impact is important.

The CRT display above the keyboard is the primary feedback to the user, and serves as a sort of scratchpad to manipulate the data to the individual's liking. Once in the right format on the screen, the data is output to a hardcopy device in exactly that format. Of course, there are certain refinements. Spectrophotometric data has certain predictable aspects. For example, since the data is acquired digitally in the 8450A, it is discontinuous, unlike the continuous data gathered by a traditional analog system. Knowing something about the information resource, however, we can apply an exact fit to the discontinuous data to fill in the gaps with a nonlinear interpolation between points. If the user prefers, a linear interpolation can be used.

Finally, the screen shows a short summary of the status of the instrument. A long form is also available. As instruments become more complex, it becomes harder to ascer-
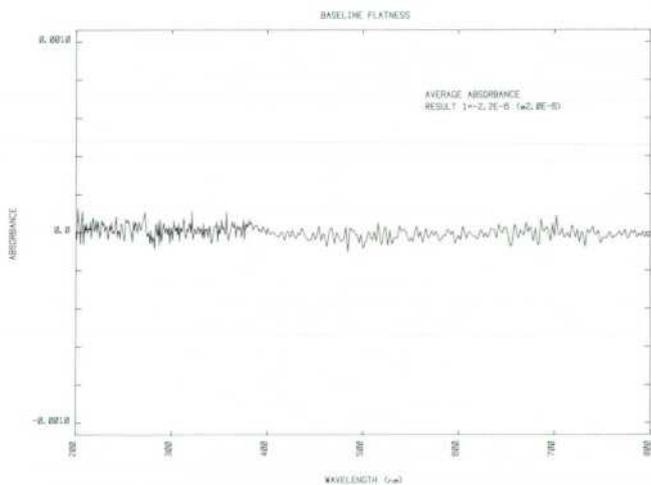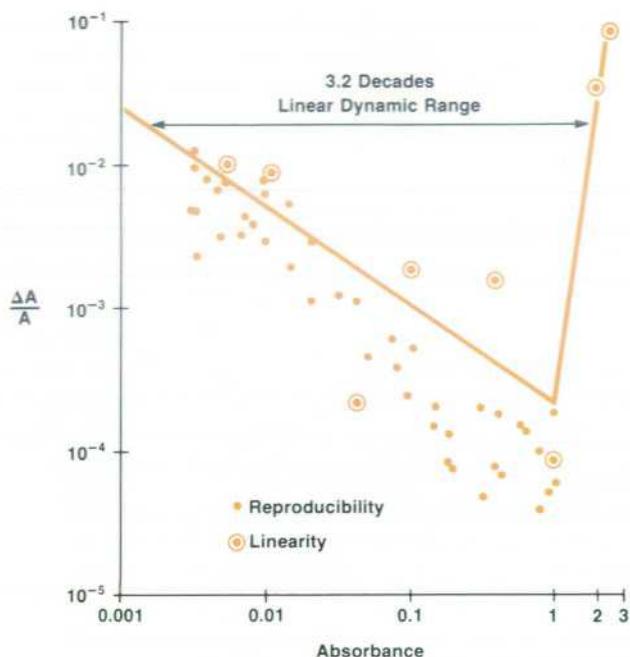
Fig. 6. *8450A fractional error in absorbance versus the actual absorbance level. The linear dynamic range for the optical system is 3.2 decades at the 2% uncertainty level. Chemical dynamic range is extended to 4 absorbance units by microprogrammed calibration.*

tain their internal state of health. The 8450A was designed with a full set of internal diagnostics that are executed at turn-on and can be called up individually for diagnosis of intermittent problems. These tests give the user confidence that the system is in a good state of health.

Performance

With a heavily integrated instrument such as this, traditional performance parameters only tell part of the story, but are a necessary starting point for the wide variety of new applications seen for this technology. Baseline performance gives an indication of the level of detectability one might expect for general low-level absorbers. This system has superior performance, as shown in Fig. 5. With an rms uncertainty better than 3×10^{-4} absorbance units (A.U.), compounds such as pyrene, a compound suspected of potent carcinogenic properties, can be detected to the level of 3.5×10^{-9} mol/l, or about 0.7 parts in 10^9 on a weight-per-weight basis. By using broadband detection techniques, an enhancement of sensitivity by an additional factor of two should be attainable. This brings the probable detection limit to better than 0.4 parts in 10^9.

The real name of the game for UV/Visible spectrophotometry is the ability to quantitate unknown concentrations of species over a reasonable dynamic range. The relationship between concentration and absorbance assumes high importance. As long as a linear assumption is made for this relationship, the absolute linearity of the photometric system becomes paramount. Fig. 6 shows a plot of the fractional error in absorbance versus the actual absorbance level. At low levels, while the uncertainty is relatively fixed in absolute value, the numeric value of the

Fig. 5. *Baseline performance is an indication of the lower limits of detectability. Model 8450A has superior performance, with an rms uncertainty better than 3×10^{-4} absorbance units.*

absorbance is approaching zero, so the fractional error is high. Even so, this level of uncertainty for such a system is very good. The next major feature is an increase in the photometric error at the higher levels. While the low-level error is based on statistical fluctuations in the data, it is the systematic error caused by the stray light of the grating spectrograph that limits the measurement at high levels. This stray light becomes dominant as the sample absorbs a significant portion of the light in a specific wavelength region.

In an electronic sense, this is the systematic noise of the system. Since the signal structure is highly variable, it is not currently considered practical to compensate for it. Finally, once the stray light becomes totally dominant, the signal information is lost, and no amount of processing will retrieve it. As it is, the total linear dynamic range for the optical system is 3.2 decades at the two percent uncertainty level. This is usually entirely adequate, since at the higher concentration levels, a chemist often has the freedom to dilute the sample to an acceptable range. Superficially, it sounds good to increase the measurement range from 3 to 4 absorbance. Actually, a large technical effort in stray light rejection is necessary to extend the intensity range by the order of magnitude required. This means increased cost, yet if the chemical dynamic range is considered to be from 3×10^{-4} to 3 A.U., increasing it to 4 A.U. only increases the chemical dynamic range by a little over 3%, which hardly seems cost-effective. However, by taking advantage of its microcomputer and programmed methods calibration, the 8450A achieves an extension of its chemical range to about 4 A.U. inexpensively, without any costly effort in stray light rejection.

At the low-level end, increasing sensitivity brings in a large number of noninstrumental factors over which we have little control. These are generally placed under the label "solution noise." In practical terms, as the race to increase photometric sensitivity heats up, the user will have to be much more precise in the selection of solvents for purity and in the treatment of the measurement containers commonly used.

Baseline stability of a spectrophotometer with time is an important factor when the procedure involved does not allow for restandardization of the optical system. Examples of this are measurements of a chemical reaction as it proceeds, or in a flow analysis situation such as liquid chro-
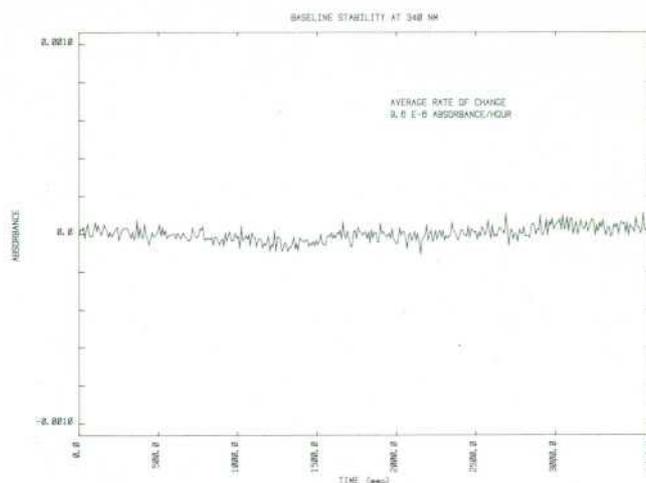
Fig. 7. *Absorbance-versus-time plot shows the 8450A's low drift.*

matography or process control streams. The 8450A system design places the critical optical elements relatively close to one another. Once control has been gained over the major factors traditionally dominant in system instability, such as beam balance and image stability of the lamps, then the thermal expansion coefficients of the materials involved begin to affect the time stability. Attention to the materials used becomes important as well as the physical layout. Since the major elements are close together, the dimensional changes are minimized and the 8450A has low drift characteristics (see Fig. 7).

Conclusion

The HP 8450A Ultraviolet/Visible Spectrophotometer adds speed, accuracy, high-level processing, and interactive capability to the overall performance capacity of photometric measurement. It allows the user to interact with the measurement problem with an ease previously impossible: to see, work with, and quantitate chemical relationships that formerly were considered impractical at best. There exists a relationship between the perceived difficulty and practicality of a given task and whether the answer to be gained is worthy of the effort. Now, for the first time, the person involved with photometric measurements can read-

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SPECIFICATIONS
HP Model 8450A UV/Vis Spectrophotometer

General System Description
The HP 8450A UV/Vis Spectrophotometer is microcomputer-controlled with keyboard entry of parameters and CRT display output. It has parallel access detection, single-stage spectrograph, dual beam (two sample stations), holographic grating. A built-in data system has 16K words storage and is programmable with 100 methods, six concentration methods. Self-diagnostic capability is included.

System Specifications
SCAN TIME: 1 second ± 0.02% full wavelength range (fastest); with time averaging, variable in 0.1-second increments to ~3600 seconds.
WAVELENGTH RANGE: 200-800 nanometers.
WAVELENGTH ACCURACY: 200-400 nm: ±1 nm, 400-800 nm: ±2 nm.
SPECTRAL BANDWIDTH: 200-400 nm: 1 nm; 400-800 nm: 2 nm.
PHOTOMETRIC RANGE: 0.0003 to 4.0 A.U. (above 3.5 A.U. linear range is extended using microprogrammed methods calibration).
REPRODUCIBILITY/LINEARITY:

A.U. at 350 nm	ΔA/A (1 s)	ΔA/A (10 s)
0.01	3%	1%
0.10	0.4%	0.15%
1.0	0.4%	0.15%
2.0	4%	4%

BASELINE FLATNESS: 0.0004 A.U. rms, 1 second.

NOISE: 0.0001 A.U. rms at 340 nm; ±0.005 A.U. p-p at 220-220 nm; ±0.002 A.U. p-p at 220-800 nm. Noise measured at 0 A.U., 10 s.
STABILITY: ±0.0005 A.U./hour at 0 A.U., 350 nm, at constant temperature.
STRAY LIGHT: Typically 5 × 10⁻⁴ at 450 nm for UV lamp.
LIGHT SOURCE: Prefocused deuterium lamp (UV region); prefocused tungsten lamp (Visible region); no mechanical switching.
DETECTOR: Diode arrays operated at ambient temperature.
DERIVATIVE: dA/dt, d²A/dt², dA/dλ, d²A/dλ².
OUTPUT PRESENTATION: Absorbance, transmission, concentration (in user-defined units) and any user-generated function.
ORDINATE EXPANSION: Autorange and manual; selectable from keyboard.
ABSCISSA EXPANSION: Variable in time and wavelength.
SAMPLE COMPARTMENT: Five sample stations capability (optional). Two sample stations supplied; open sample compartment for easy access to multiple accessories.

Data System Specifications
MICROCOMPUTER: 16-bit word with 28K operating system and 16K words of user memory supplied. (Extra 16K words of user memory, optional.)
NUMERIC RANGE: 2E-39 to 1E+38.
PROGRAMMABILITY: Keystroke programming for up to 100 methods. 20 lines each, 10-deep nesting.
QUANTITATIVE METHODS: Least squares maximum likelihood statistics. Two linear methods (zero and nonzero intercept), two second-order methods (zero and nonzero

intercept), kinetic method, and multicomponent analysis (7 components over full wavelength range, 12 components over limited wavelength range).
CONTROLLER INPUT/OUTPUT: Controls external peripherals and allows data input and output over serial (RS-232C) and parallel (HP-IB, IEEE 488-1978) interfaces.
DIAGNOSTICS: Microcomputer-controlled self-diagnostics.

Environmental Specifications
TEMPERATURE: Operating 0° to 40°C; non-operating, -40°C to 50°C; rate of change not to exceed 10°C/hour.
RELATIVE HUMIDITY: 5% to 80% (non-condensing). Wet bulb temperature <40°C.
DIAGNOSTICS: Microcomputer controlled self-diagnostics.

Utilities, Dimensions, Weight
POWER LINE SPECIFICATIONS: 100, 120, 220, 240 volts ac, each +5%, -10%.
FREQUENCY: 50 Hz +10% -5%; 60 Hz ±10%.
PHASE: Single.
POWER: 225 watts typical. Current at 120V, 60 Hz: 2.4 amperes typical.
UNIT SIZE: 890 mm W × 270 mm H × 610 mm D.
NET WEIGHT: 44 kg (97 lb).
PRICE IN U.S.A.: $21,500.
MANUFACTURING DIVISION: SCIENTIFIC INSTRUMENTS DIVISION
1601 California Avenue
Palo Alto, California 94304 U.S.A.

ily see the interrelationships of the various chromophores present and easily determine whether sufficient chemical information can be retrieved from the system to solve the problem at hand. This kind of closed-loop, interactive relationship with the chemical problem allows a more creative

and productive approach to analysis than was previously possible. This means that the basic speed and productivity of photometric measurements can be brought to bear on a much wider range of problems than was thought possible before this development.
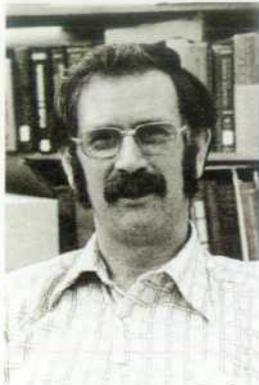
Barry G. Willis

With HP since 1970, Barry Willis worked on the entire development of the 8450A Spectrophotometer, contributing many concepts and serving as project manager. A native of Seattle, Washington, Barry graduated from Oregon State University in 1963 with a BSc degree and earned his PhD from Purdue University in 1970. He's active in the American Chemical Society (he's local chairman of the ASC professional relations committee), has written ten papers, is named inventor on three patents in the instrumentation field, and has taught quantitative analysis, general chemistry, instrumental analysis, and computers in chemistry. He and his wife and 12-year-old son live in Los Altos Hills, California. Barry sings in his church choir, creates stained glass, hikes, and occasionally participates in city council activities. Currently he's using his carpentry skills to renovate a 53-year-old farmhouse.

Gerald E. James

Jerry James is an applications chemist currently providing sales support for the 8450A Spectrophotometer. He received his BS degree in chemistry from the University of Alabama in 1965 and his PhD degree in analytical chemistry from Purdue University in 1969. After two years developing a GC/MS data acquisition system, he served as an assistant professor at Clemson University for a year, teaching analytical chemistry of water and waste water. Then for the next seven years he was R and D manager for a microprocessor-controlled system for following the kinetics of immunochemical reactions. He joined HP in 1979. Author of three papers, he's a member of the American Chemical Society and the American Association for Clinical Chemistry. Born in Murfreesboro, Tennessee, Jerry is married and lives in San Mateo, California. His interests include basketball, tennis, photography, and hiking.

A Task-Oriented Approach to Spectrophotometry

by Arthur Schleifer and Barry G. Willis

THE DESIGN of any keyboard-operated instrument usually involves a tradeoff between simplicity for the inexperienced or casual user and versatility for more sophisticated users and measurements. The firmware control programs for the 8450A UV/Vis Spectrophotometer are designed to perform a wide range of operations with the measurement complexity transparent to the user. The natural language of the chemical environment has been maintained to facilitate communication of measurement tasks from the user to the instrument.

The 8450A is designed to allow the user to get answers to chemical problems rather than just generate photometric data. Thus it represents a task-oriented approach to UV/Vis spectrophotometry. The user enters the measurement procedure, specifies the data reduction and display parameters, and obtains answers in the desired format.

User Communication

It was a major goal of the 8450A design team to make the

human interface to the instrument as friendly as possible, yet still retain the ability to do a variety of highly complex tasks. A number of approaches were considered. A fully instrument-oriented approach, with the various parameters of the measurement setup entered one at a time, seemed too restrictive and noncommunicative. A menu approach, with a list of questions or options to be selected for the measurement task, seemed communicative but was too slow in practice if only minor modifications were desired. The approach selected is user-oriented, with a sentence structure input. This approach seemed most natural and versatile, and is very fast for minor data modifications.

The command formats are designed to accomplish a basic set of tasks:

1. Data transfer and formatting
2. Output of operational information (labels)
3. Plotter or device parameter setup
4. Variance format control
5. Interrogation of status
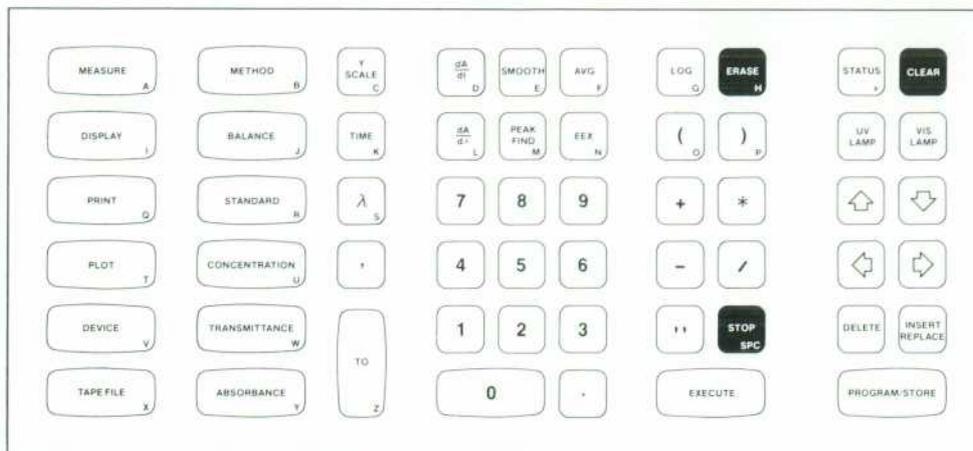
Fig. 1. *8450A keyboard is arranged so that the general flow of a command sequence is from the upper left to the lower right.*

6. Clearing from memory of standards, methods, or balance
7. Initiation of a method run
8. Pause during a method.

The general form of a command is as follows.

[SOURCE] [TO] [DESTINATION(S)] [CALCULATION PROCESS]
[DISPLAY PARAMETERS] [EXECUTE]

To make the entry of commands efficient, the keyboard (Fig. 1) is arranged so that the general flow of a command keystroke sequence is from the upper left to the lower right of the keyboard, terminating with the EXECUTE key.

As keystrokes are entered, they are echoed on the CRT screen (Fig. 2). Error checking occurs with each entry. If an entry error is detected, the system moves a cursor to the offending entry, beeps, and displays an explanation of the error (Fig. 3). To correct errors, the cursor can be moved in and out of the line and keystrokes inserted, deleted, or replaced.

There are two basic statement types: explicit and imperative. An example of the explicit entry of a command might be:

DISPLAY TO PLOT ABSORBANCE λ 350 TO 700 EXECUTE

In the imperative form, the source and destination are inferred without the use of the TO key. An example to perform the same operation is:

PLOT ABSORBANCE λ 350 TO 700 EXECUTE

This flexibility in the command format promotes a friendlier interaction with the system.

Calculation process and display parameters are defaulted to most likely values at turn-on and their most recent entries are maintained until specifically modified. Therefore, the example above could have been:

PLOT EXECUTE

The 8450A is largely a state-operated machine. This means that operational definitions are set up and sequenced through regardless of the keyboard entry order. Thus the user can define an operation in essentially any order or level of detail.

The calculation process entry can be as simple as the absorbance value or somewhat more complex. An example is the direct calculation of pH from the spectral measurement of a pH-sensitive dye:

MEAS (7.22 + 1.121 * LOG (ABS 426 TO 440/ABS 554 to 566))
EXECUTE

This command line specifies that a measurement be made and the average absorbance from 426 to 440 nm be divided by the average absorbance from 554 to 566 nm. The logarithm of this result is calculated and multiplied by the value 1.121, and 7.22 is added to the result. Statistical error analysis is done automatically for each measured value and each computed result. This flexibility in the command process allows the user to tailor the data processing to specific applications.

In addition to single-line commands, the 8450A can store several command lines as a method. When executing a method, the 8450A sequentially steps through the stored command lines, which may include audible and visual prompting for the operator. This allows complex operations to be executed with a single keystroke sequence. As many as 100 methods, each with up to 20 lines, can be stored. Methods can also be edited and saved in memory or on
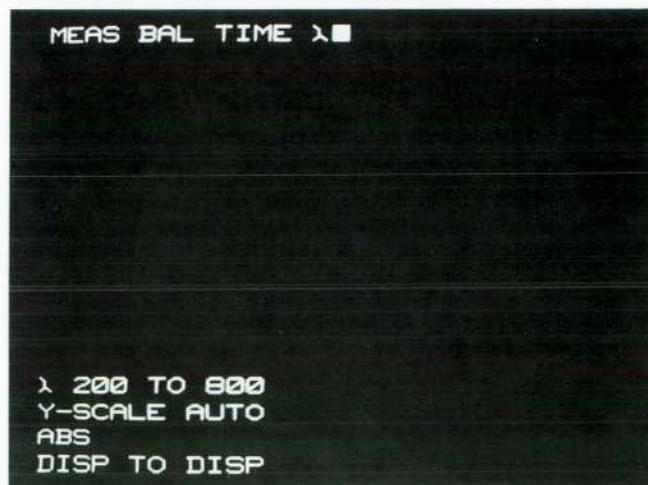
Fig. 2. *Keystrokes are echoed on the CRT.*

```
MEAS ABS TIME λ 250 TO ▮45
645 ?
wavelength > 400 must be even




λ 200 TO 800
Y-SCALE AUTO
ABS
DISP TO DISP
```
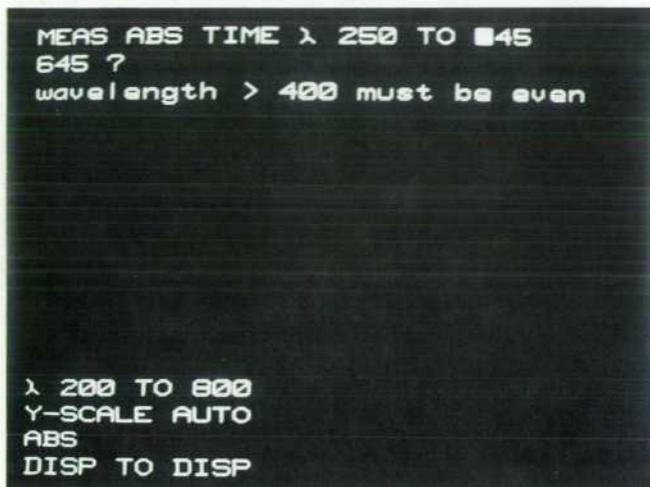
Fig. 3. *An entry error causes the system to beep and display an explanation of the error.*

cartridge tape for subsequent use.

Optical Measurements

The optical measurement data acquisition section of the 8450A operating system firmware controls the position of the beam director, sets the gain of the photodiode array preamplifier, reads the data, and performs the measurement calculations. The data acquisition module consists of four submodules that are coupled only by status flags and data storage areas and do not jump to or call one another. Each submodule is either called by other sections of the firmware or executed when an interrupt occurs. The first submodule, measurement initialization, is called at power-on to initialize status flags and parameters used by the other measurement submodules, and is not called or executed at any other time.

The second submodule, measurement control, determines the sequence of data acquisition operations. The diode array clocking circuitry sends a series of interrupts to the system at 100-millisecond intervals, and this submodule determines the procedure to be executed when the next series of diode array interrupts occurs.

The data acquisition module, the third submodule, is entered when the diode arrays interrupt. Since each diode has a gain value associated with it, the first operation is to write the next gain value to be used by the hardware. Then a value from the analog-to-digital converter is read and some preliminary calculations are performed before storing the results in a data buffer. These calculations can be any of five different types, depending on the control information set up by the measurement control module. After processing the data from a single diode, control is returned to the program that was interrupted.

The program execution time of the data acquisition submodule is extremely critical to the performance of the 8450A. When the diode arrays are interrupting to be serviced, the time between individual diode interrupts is only 125 microseconds. The calculations required, if done in software, would take longer than the time between interrupts. To increase the speed of the calculations, a sixteen-bit hardware multiplier is used. With the hardware multi-

plier, the calculations take between 60 and 80 microseconds. This still does not leave much time before the next interrupt occurs. In addition, each time a diode array interrupts to request service, the system must respond to the interrupt and write the next gain value to the hardware within 62 microseconds or an error condition will occur and the subsequent data will be invalid. These constraints made it necessary to develop an extremely efficient interrupt service procedure.

By keeping the external register base of the MC5 processor* set to the diode array register base whenever the interrupt system is on, the interrupt service routine saves the time necessary to read the current register base, store it in a memory location, and set up the required register base. The priority encoding feature of the MC5 processor enables the system to select the appropriate service routines within one instruction after reading the external interrupt status register. The entire software overhead for an interrupt, including saving the current status to free an internal register for use and selecting the service routine, is only 10.4 microseconds. To be sure that the diode array is completely serviced, the interrupt system is turned off to assure that other interrupts do not interfere and cause the processing interval to exceed 125 microseconds. This is allowable because the diode array has the highest priority of all interrupts.

Measurement Calculations

The measurement calculation routines, which are in the fourth submodule, are an innovative feature of the new UV/Vis spectrophotometer. Not only are the results calculated from the raw data, but the uncertainty or standard deviation of the results is calculated as well. This is the first commercially available analytical instrument that tells the user how much confidence should be placed in the results it is reporting.

Each data point is made up of a series of measurements for which the average value is computed. Instead of simply summing the data, the system stores the first value, then sums the differences between the first and subsequent values in another location until the integration time is complete. The purpose of this is to acquire the necessary sum without the danger of possible overflow conditions for long integration periods. The equation for the average then looks like this:

$$\bar{x} = x_1 + \frac{1}{n} \sum_{i=1}^{n} (x_i - x_1)$$

At the same time the sum of the squares of the differences is stored for the variance calculation. We now have the sum of the differences and their squares for the variance equation:

$$\sigma^2 = \frac{1}{n^2 - n} \left\{ \sum_{i=1}^{n} (x_i - x_1)^2 - \frac{1}{n} \left[\sum_{i=1}^{n} (x_i - x_1) \right]^2 \right\}$$

This is the basis for the calculations done on all data ac-

*The MC5 processor is a 5-volt version of HP's silicon-on-sapphire MC² (see reference 1). The register base of the MC5 is an eight-bit register that is used to keep track of banks of external registers during input/output operations. External devices, such as the diode arrays, each have one or more eight-register banks. Only one of a possible 256 banks may be accessed at any time, and the register base specifies which one.

quired, including sample, reference, and dark current measurements.

To initialize the entire measurement sequence at turn-on, the beam director is commanded to find and verify the presence and positions of the installed cube-corner reflectors. With this information available, and having verified that there are at least two cube corners present, the system then adjusts the preamplifier gain value for each diode such that the measured intensity is in an optimum range for the analog-to-digital converter (ADC). After the turn-on sequence or a measurement sequence, while the system is waiting for a command input, it takes a series of dark current measurements. With the beam director in resting dark position and no signal light falling on the arrays, sixteen frames of dark current information are integrated into a sliding average. This average of the latest sixteen frames of dark current signal is then subtracted from the sample/reference measurements to reduce the contribution of the dark current noise to the overall measurement uncertainty.

Most systems either require matched or very minimally different sample and reference paths so that they can achieve good common mode rejection and flat response as a function of wavelength. In practice, this is impossible to maintain. The 8450A achieves better performance by actually measuring and storing the degree of optical balance. This balance information is updated on demand. The user puts both the sample and reference paths into a reference state, for example by installing two sample cells (cuvettes) that both contain solvent. The keyboard sequence MEASURE BALANCE EXECUTE causes the system to measure the two paths and calculate the ratio between them. This ratio is stored in a buffer for later use. The equation is

$$B = \log_{10} \frac{S' - D}{R - D}$$

where B is the optical balance, S' is the sample path measurement with the sample path in a reference state, R is the reference path measurement, and D is the dark current measurement.

The error analysis is also carried out and stored as the statistics of the balance. Usually, the balance is measured for a period longer than the sample measurement to minimize the impact of its uncertainty on subsequent absorbance measurements.

Measurement Sequence

The actual measurement sequence is determined by the measurement control submodule from the parameters specified in the user command. For a one-second measurement, the beam director starts from the resting dark position. It is commanded to move to the sample position, and when the system verifies that it is there, the sample integration begins. When complete, the beam moves to the reference position, and after verification of a successful move, the integration cycle for the reference path is initiated. After the sample and reference measurements, the beam is returned to the dark position and one additional dark measurement is made for the 16-frame running average.

While new data is being acquired, the statistical information is calculated for the cycle just completed. When all the measurements have been taken, the final calculations for absorbance and statistics are initiated.

$$A = -\log_{10} \frac{S - D}{R - D} - B$$

A fast table-lookup algorithm for the calculation of logarithms with interpolation for the necessary precision is used to attain the speed required to complete the calculations for all 401 wavelength values and their statistics within one second.

This process provides the mean value for the absorbance and the estimated variance about the mean value. To reduce the amount of memory required to store both pieces of information, a special two-word compressed number format was developed. The format allows for more than the necessary precision in the absorbance range and sufficient resolution for an accurate representation of the standard deviation σ.

Data Processing

Once the absorbance data from the measurement has been calculated, the user may want to process the data further to obtain the results in a format suitable for a particular application. This function processing can include wavelength or time-dependent functions as well as functions resulting in a single number. The function command can refer to absorbance, transmittance, or a mixture of measurement data and arithmetic operations.

Before processing the data, the firmware performs a series of checks for compatibility of the source of the data, the function to be calculated, and the destination of the calculated results. After the function processing, any of several post-function calculations may be specified. These include: PEAK-FIND, SMOOTH, AVERAGE, and CONCENTRATION.

When a spectrum is displayed on the CRT, the cursor arrows on the keyboard may be used to search the spectrum for maxima. This can also be accomplished by use of the PEAK-FIND function. Depending on the wavelength limits and the signal-to-noise ratio of the data, PEAK-FIND will locate up to thirty peaks or valleys in the spectral data and provide a tabulation of these results.

The measurement of very small signals in the presence of random measurement noise can be a problem. The ability to smooth or filter the data is a key element in being able to extract information from an otherwise unusable spectrum. A Savitsky-Golay algorithm[2] is employed in the 8450A, and the number of data points for the SMOOTH function can be specified by the user (from 5 to 25).

The AVERAGE function, as it implies, calculates the average of a specified range of data. It can be used to increase the signal-to-noise ratio of a measurement: data from several wavelengths can be averaged, effectively increasing spectral bandwidth, to provide data that is less sensitive to instrument noise. When applied to the first time derivative, the AVERAGE function provides the average rate of change of time-dependent measurement data. This information can be used in further kinetic calculations, such as activity coefficients of enzymes.

A primary function of a UV/Vis spectrophotometer is the determination of concentration, or how much of a particular solute is in a sample. 8450A concentration calculations

are all based on Beer's Law, which states that concentration of a sample is proportional to its measured absorbance value:

$$C = KA$$

where C is the concentration of the sample, A is absorbance, and K is a proportionality constant given by

$$K = 1/(\text{absorptivity} \times \text{sample path length}).$$

The concentration of a sample is usually measured relative to the measurement of a known concentration of a prepared sample. Since the ratio of concentration to absorbance for the unknown sample and the standard are equal, the concentration of the sample is calculated as follows:

$$C_u = \frac{A_u \times C_s}{A_s}$$

where C_u is the concentration of the unknown sample, A_u is the absorbance of the unknown sample, C_s is the concentration of the known standard, and A_s is the absorbance of the known standard.

This type of calculation is the traditional procedure for calculating the concentration of a single solute in solution. The command CONCENTRATION 0 calls for this calculation, but also allows the user to improve the precision of the calculation by using several standards at different concentrations. Here the 8450A differs significantly from traditional instruments, using parameter estimation methods to estimate the most likely straight-line fit when more than one standard is specified.

In the real world of chemical spectrophotometry, there are deviations from Beer's Law. These can be caused by chemical interactions or by instrument nonlinearity at high absorbance values. CONCENTRATION 1 through 3 specify routines that allow the user to compensate for these deviations. Whereas CONCENTRATION 0 specifies a straight-line fit with an intercept through the origin (Beer's Law), CONCENTRATION 1 allows for some fixed offset from the origin by adding a term to the Beer's Law equation:

$$C = K_1 A + K_0$$

where K_0 is the offset from the origin.

CONCENTRATION 2 corrects for nonlinearities but still forces the intercept through the origin. The equation for this routine is as follows:

$$C = K_2 A^2 + K_1 A$$

where K_2 is the second-order curvature.

Finally, CONCENTRATION 3 provides correction for both nonlinearity and a fixed offset from the origin by the following equation.

$$C = K_2 A^2 + K_1 A + K_0$$

The K values in the above equations are estimated by an algorithm that fits a line to the values from the standards. This is actually a two-step procedure consisting of a first pass that estimates the parameters (K_0, K_1, K_2) using an ordinary least-squares fit.[3] Then, using the uncertainty of the standards, a second estimation is made using a maximum-likelihood method.[3] When the curve is fitted to the values of the standards, the higher-accuracy standards are weighted more heavily so they exert more influence on the curve. The curve-fitting process computes the estimates of the K values and the errors in the K values, and takes any covariance between them into account. These estimated K values are then used with the measured absorbance to calculate the concentration. The errors are also combined to estimate the uncertainty or confidence level of the concentration results.

The user can determine which concentration method should be used for a particular series of standards with the STATUS CONCENTRATION (0 through 3) procedure. STATUS CONCENTRATION does the calculations for the estimation of the K values and displays these values on the CRT. The percent deviation from the calculated curve for each standard will also be displayed. The user can very quickly try each concentration procedure to determine which has the least deviation from the calculated calibration curve.

Multicomponent Analysis

One of the limitations of conventional spectrophotometry is that a relatively pure sample has always been needed to measure concentration. This necessitated additional chemical preparation of the sample before the analysis. The 8450A does not have this limitation.

Beer's Law, which says that absorbance is proportional to the concentration of sample in the light path, is also true when there is more than one absorbing species in the same solution. The total absorbance can be described as follows:

$$A = b \sum a_i C_i$$

where A is absorbance, b is sample path length, a_i is the absorptivity of species i, and C_i is the concentration of species i.

Two basic conditions must be met before the 8450A can calculate the concentration of a multicomponent mixture. One is that all of the absorbing species must obey Beer's law. The other is that all the components in the mixture have been identified as standards. The procedure for a multicomponent analysis is simple. First, a spectrum of a known concentration of each species is measured. The results are stored in the 8450A as standards (for example, standards 1, 2, and 3) along with their concentrations. A mixture of these species can then be measured and the concentration for each component calculated by simply entering the keystroke sequence:

MEASURE CONCENTRATION 4, 1 TO 3 EXECUTE

The calculated results will be displayed on the CRT in a few seconds. The 8450A performs the calculation by finding the proportions of each standard that best match the unknown spectrum over the entire data range specified by the user.

Traditionally, the concentrations for multicomponent systems are calculated by solving a series of simultaneous equations equal to the number of components in the mix-

ture. The user must carefully select the data points for the analysis. In the 8450A, the user simply selects a data range and the parameter estimation techniques weight the data points proportionally to the variances of the standard and the unknown measurements. Hence, where the precision of the measurements is very good, the data will be weighted more heavily than where the precision is poor. The 8450A overdetermines the system (more data points than unknowns), and provides three additional pieces of information to inform the user about the performance of the multicomponent calculation. They are relative fit error, independence of standards, and relative standard deviation of each component. The relative fit error is an indication of how well the algorithm was able to fit the unknown measured curve to the sum of the standards generated by the computer. An increasing relative fit error is an indication of some form of analytical problem. The independence of standards is a measure of the orthogonality of the specified standards. As the individual standards become less and less unique, the multicomponent algorithm has greater difficulty distinguishing between them. This can lead to errors in quantitation of the individual components. Since all of the computed uncertainties are carried through all of the calculations for concentration, the relative standard deviation of each component can also be provided. These three additional pieces of information help the user monitor the performance of the multicomponent procedure. Traditional multicomponent techniques do not provide this information, so analytical problems may go unnoticed.

All of the concentration routines on the 8450A work with both wavelength-dependent and time-dependent (kinetic) data. This provides the exciting capability of quantifying components of a mixture of simultaneous kinetic reactions.

Information Display and Peripheral Communication

The primary device for the display of results and information is the CRT. The CRT display can show alphanumeric information and up to two graphic plots simultaneously (Fig. 4). In addition, the user can communicate with external devices for generating a hard copy of results or saving data and methods. Communication with a remote desktop computer or larger computer is also possible. Communication is established by connecting these devices to either the HP-IB (compatible with IEEE 488-1978) or the RS-232C connectors on the rear panel of the instrument. The CRT allows the user to manipulate the data and format the results before sending the data to an external device. This scratchpad aspect of the CRT display saves time and material (paper, etc.).

A common form for the data is a spectrum, which is a series of plotted data points. Once the user has specified the display limits of the spectrum, the command PLOT EXECUTE causes the spectrum to be transferred for hard copy. Plotting can be done by any one of three HP-IB plotters: the HP 7225A X-Y Plotter, the HP 9872 X-Y Plotter, or the HP 7245A Plotter/Printer. When the PLOT EXECUTE command is executed, the firmware will determine which plotter is connected and use the appropriate programs. The firmware will also take care of the necessary HP-IB protocol so that the user requires no intimate knowledge of the interface. After the spectrum is plotted, the user can label the plot
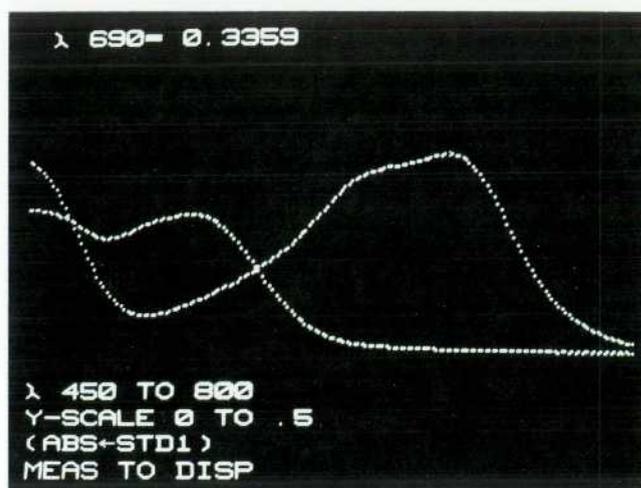
Fig. 4. *CRT can show two plots simultaneously along with alphanumeric information. Data can be corrected and formatted on the CRT before being sent to a hardcopy device.*

with the PLOT "..." command. When this command is executed, the user-entered string (in quotes) is printed at the top of the plot and the axes are drawn and labeled. Additional enhancements to the plots can be made, such as annotations of data points, interpolated or noninterpolated plotting, pen color selection (9872 only), selection of seven different line types, and other plot formats.

If a hard copy of alphanumeric data is required, the PRINT command transfers the information from the CRT to a printer. As with the PLOT command, the PRINT program searches to find an HP-IB printer. If there is no HP-IB printer, the program tries to print the information on a plotter. The information can also be directed to the serial interface when an RS-232C printer is available.

The HP 9875A Cartridge Tape Unit can be used to store data generated by the 8450A. It can also be used to store programmed methods for use with the 8450A.

Decision making, or an IF THEN statement, is not a capability of the 8450A, but can be accomplished through communication with a remote computer. The remote computer can receive data through the RS-232C interface port

Arthur Schleifer

Born in New York City, Art Schleifer joined HP's Avondale, Pennsylvania, Division in 1974, working on gas chromatograph accessories. Now with the Scientific Instruments Division, he helped define the user interface of the HP 8450A UV/Vis Spectrophotometer and was responsible for the software for the I/O and peripherals. Art received his BS degree in chemistry from York College of the City University of New York in 1971 and worked in the analytical laboratory of a major pharmaceutical company for three years before joining HP. Living in Palo Alto with his wife and two sons, he spends some of his leisure time building furniture, golfing, playing tennis, and using a home computer.

port either in ASCII characters or in the 8450A's internal data format (two-word compressed format). The remote computer can also completely control the 8450A by sending commands via the interface. This allows the computer to make decisions about further measurements based on the transferred data.

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An Optical System for Full-Spectrum Measurements

by George W. Hopkins and Alfred Schwartz

A MEASUREMENT SYSTEM is only as good as the basic transducer. In a modern spectrophotometer, that transducer is an optical system with an electro-optical detector.

Design of an optical system for the 8450A UV/Vis Spectrophotometer posed certain special problems, since conventional configurations did not provide adequate speed and quality. It was recognized from the start that a serially scanned monochromator with mechanical drive would be at least two orders of magnitude too slow at the scan rates

necessary to provide an acceptable signal-to-noise ratio. The approach taken was to adopt newer technology, specifically photodiode arrays in combination with holographically recorded diffraction gratings. These gratings use aberration compensation to image sharp spectra onto the photodiode arrays. Other modern techniques, such as servo systems for image positioning and replication* of

*Replication is the process of transferring the optical form from a precision master mirror to a relatively inexpensive machined part. A thin layer of epoxy cement is used to fill in differences between the machined part and the desired surface.
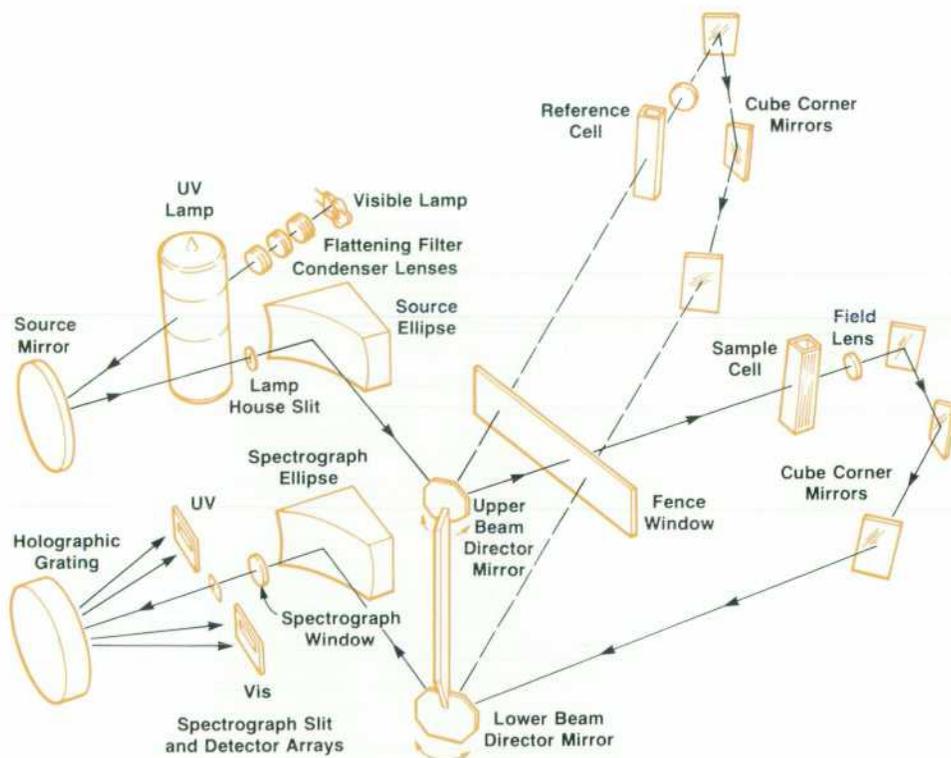
Fig. 1. The folded optical system of the 8450A Spectrophotometer.

exotic optical surfaces, are also used. The result is an instrument with highly desirable performance levels and speeds that were only dreams for the chemical community a few months ago.

Optical System

The optical system, pictured in Fig. 1, is divided into three principal sections. In the source section, two light sources are combined and focused on a source slit. In the sample section, two confocal elliptical mirrors relay the light from the source slit through the sample, which is at the common focus of the ellipses, to a second (spectrograph) slit. In the spectrograph section, the light from the spectrograph slit is diffracted into spectra by a holographic grating and then detected by diode arrays.

The first element in the source section is a 20W tungsten-halogen lamp. Its filament is imaged through a spectral flattening filter onto the aperture of a see-through deuterium lamp. Two standard infinity-corrected achromats, used face-to-face, form the condenser lens.

The tungsten flux combines with the deuterium flux, and the deuterium-arc/tungsten-filament image is then reimaged onto a 0.120-mm-by-0.600-mm source slit. A replicated ellipsoid with the lamp at one focus and the slit at the other focus serves as the condenser mirror.

In the sample section the source slit is imaged into the sample area by another replicated ellipsoid at 7.4 magnification.

Two flat mirrors on a common shaft move the light beam to different sample positions. The shaft rotates about an axis perpendicular to the plane defined by the sample section ellipsoid foci. The shaft is under control of the computer and a servomechanism (see article, page 24). The shaft, its mirrors, and the associated mechanical and electronic parts are called the beam director—the only moving part in the optomechanical system.

Light diverging from the common ellipsoid focus at the sample cell position strikes a field lens, which is located as close as mechanically feasible to the sample position. This field lens images the first sample section ellipsoid onto the second sample section ellipsoid to reduce clear aperture requirements at the second ellipsoid and to increase flux through the system.

Next are three flat mirrors. The mirrors form a cube corner whose diagonal intersects the beam director shaft midway between the centers of the two beam director mirrors. The cube corner returns the entering beam back along the direction it entered. The returning beam lies parallel to the entering beam, but on the opposite side of the cube corner diagonal and equidistant from it. The vertex of the cube corner is located at the proper distance to allow the sample area image to be focused onto the spectrograph slit when a 10-mm sample cell with aqueous solution is in the beam.

After reflection from the lower beam director mirror, light is focused onto a 0.05-mm-by-0.500-mm slit by the second sample section ellipsoid, which is identical to the previous one. A high-quality image of the 0.120-mm-by-0.600-mm source slit is formed on top of the spectrograph slit. The slit jaws are chisel mirrors tilted at 15 degrees to direct light from the sides of the image onto photodiodes on each side of the entering beam. These diodes provide a signal for the

servomechanism that controls the beam director shaft location by balancing signals from the two diodes (see page 24).

In the spectrograph section, light passing through the slit strikes two holographically recorded diffraction gratings. These gratings have semicircular boundaries with a vertical line of separation. They are formed on a common substrate. The grating lines are tilted at 3.5 degrees to the vertical to separate their spectra. A photodiode array is positioned at the first-order spectrum of each grating. These arrays each use 200 elements. One grating, the UV grating, covers 200 nm to 400 nm, and the other grating, the Vis grating, covers 400 nm to 800 nm.

Absorption filters are located over appropriate portions of the diode arrays to eliminate signals from second-order spectra. The negative-order spectra strike a blackened surface beneath the arrays as a result of the tilted grating lines. The grating substrate is at a 0.75-degree angle horizontally with respect to the incoming beam to cause the zero-order spectral line to strike a blackened surface to one side of the slit.

Three windows protect portions of the optical system. The first is located after the upper beam director mirror. This is a long rectangular fused-silica piece similar to a microscope slide. It is perpendicular to the beam at the central sample cell position and is called the fence window. The fence window and the field lens, which serves as a second window, isolate the sample area from the interior of the instrument. A thin fused-silica disc is located just before the final slit to permit sealing of the spectrograph.

Measurement Cycle

The 8450A Spectrophotometer makes relative measurements, as do all spectrophotometers. As a preliminary step, a balance spectrum is taken, with identical sample cells containing solvent at the reference and sample positions. The differences in counts between the two positions are stored. Then the cuvette at the sample position is emptied of solvent and filled with the solution to be measured. The beam is again steered between the two positions and spectra are taken. The microcomputer then calculates a sample-to-reference ratio and corrects for the balance spectrum and a dark current spectrum to determine the absorbance spectrum of the sample.

During each measurement cycle, the microcomputer steers the beam director to an address where it found a cube corner during startup. This places the beam onto the spectrograph slit. The beam director servo system locks the beam onto the slit and holds it there within three seconds of arc while the detector diodes integrate the signal and are read out. The computer then steers the beam director to the next address and the cycle is repeated.

Design Philosophy

Some challenging engineering problems had to be solved to make the 8450A a reality. An optical system was required that could provide data at a rate that would complement the computing power available. This required invention and substantial subsequent development work, often in cooperation with our vendors. The guiding principle was maximum exploitation of state-of-the-art technology.

Our basic engineering philosophy was to provide cus-

tomers with a reliable and easily repairable instrument. Specific design objectives :

- The optical system would be integrated with other systems to obtain the performance and speed desired.
- Field adjustments in the optical system would be minimized to simplify user maintenance and field repair. Factory adjustments would be made as required to obtain maximum performance margins.
- Modularity would be achieved at the lowest possible level to reduce repair costs and speed repairs.
- The system would be packaged for compactness, ruggedness, and ease of external access by the user.

Design Problems

The source section must produce a spectrum of energy from 200 to 800 nm without switching lamps during a measurement. This requires combining of the beams from two light sources and is accomplished with a see-through ultraviolet lamp. Refractive elements cannot be used after the ultraviolet source, so a replicated source (condenser) mirror with an ellipsoidal surface is used to provide the spatial and spectral uniformity required in the beam.

The relay optic must transfer an image of the source slit into the sample and then onto the spectrograph slit so that variations in the flux passing to the grating caused by anything other than absorbance in the sample are less than one part in ten thousand. To achieve this, the beam director must position the source slit image accurately on the spectrograph slit. If the beam image is highly uniform, an acceptably low variation in flux will be achieved at a less accurate level of beam director repeatability. Analysis of this problem required development of a theory to relate performance (flux variation) to optical component quality and alignment.[1] Once this theory was available, system performance was analyzed at different levels of modularity, starting at the component level. This process continued until an acceptable compromise was achieved for the level of field assembly replacement, the expense of making ad-

justments, and a suitable margin for residual misalignment of components. The result is that most optical components are factory adjusted to midlevel assemblies and are fixed in place, insuring accurate and rugged alignment while still permitting replacement of modules with moderate cost.

The spectrograph contains a diffraction grating with fine, almost straight, almost parallel lines that diffract or disperse light at different angles depending on the wavelength of the light. This grating also reimages the spectrograph slit, which is the same size as individual diodes in the photodiode array, onto the diode array. Because of dispersion, light of different wavelengths forms images of the slit on distinct diodes. Two problems occurred in the design of the spectrograph. The instrument covers two octaves, that is, 200 nm to 400 nm and 400 nm to 800 nm. If a single grating were used, the spectra generated by light from 200 nm to 400 nm would overlap spectra generated by light from 400

Alfred Schwartz

Fred Schwartz developed a confocal ellipse system for use in the 8450A Spectrophotometer and helped design the illumination and overall optics. Born in Romania, he earned a Diploma Engineer degree in 1953 from Bucharest Polytechnic Institute and a BS degree in physics in 1955 from the University of Bucharest. A member of the Optical Society of America, the Society of Photo-Optical Instrumentation Engineers, and the American Institute of Physics, he has contributed optical designs to the U.S. moon lander, space shuttle, and other programs, has written many papers on optical topics, and has generated two patents in the same area. Fred now lives in Mountain View, California. His interests include international folk music, stereo photography, movie making, and traveling and snorkeling in the South Pacific. He's been with HP Laboratories since 1972.

Holographically-Recorded Diffraction Gratings

The holographic grating in the 8450A Spectrophotometer is produced by placing a photosensitive coating on an optically polished spherical substrate. This coating is exposed by a strong laser beam that is split in two and directed onto the coated substrate from two specific points.

Interference fringes are formed in the space where the recombined beams overlap. The bright fringes expose the photosensitive coating, and with development, grating grooves form at the fringe locations. When the developed coating is given an overcoating of aluminum, a diffraction grating results. A replication technique similar to that used for the ellipsoidal components is used to produce less expensive gratings from holographically-recorded master gratings.

Aberration correction of the gratings is a result of proper choice of the directions and divergence points of the beams from the laser.

Reference
1. "Handbook of Diffraction Gratings Ruled and Holographic," Jobin-Yvon Division, Instruments, S.A.

George W. Hopkins

George Hopkins was optical engineer on the 8450A project from lab prototype to production release. He holds a BA degree in physics and German from the University of the South (1968), an MS in physics from the University of Massachusetts (1970), and MS and PhD degrees in optical sciences from the University of Arizona (1975-1976). Formerly a research associate and manager at the Optical Sciences Center of the University of Arizona, George joined HP in 1977 to work on the 8450A Spectrophotometer. Active in the Society of Photo-Optical Instrumentation Engineers and the Optical Society of America, he's authored five professional papers, organized and chaired conferences, and taught optical engineering. George was born in Sewanee, Tennessee and served in the U.S. Air Force for three years. He's married, has a small daughter, and lives in Sunnyvale, California. His interests include amateur radio and making telescopes.

nm to 800 nm because a diffraction grating forms multiple spectra. Second, aberration can be compensated at one wavelength only and will increase with increasing difference of wavelength from the compensated wavelength. Third, grating efficiency would decrease to unacceptably low levels if a single grating were used to cover two octaves. These problems are solved by using two gratings on the same substrate. One grating covers 200 nm to 400 nm and the other covers 400 nm to 800 nm. Aberration can now be corrected at two wavelengths (one for each grating), each grating covers one octave only, and the gratings can be tilted slightly so that the multiple spectra from one grating will not overlap the main spectrum from the other grating.

Conclusion

The optical system permits a full-spectrum measurement in one second and attains a performance level not found in earlier instrumentation. The instrument particularly excels in measurements at very low absorbance levels as a result of its short measurement cycle (contributing to stability) and the care used in design and assembly of the optical system.

Reference

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Light Detection and Measurement in a High-Performance Spectrophotometer

by Knud L. Knudsen and Robert W. Widmayer

THROUGH THE USE OF HIGH-TECHNOLOGY electronic systems, a great deal of the cost and complexity of an optomechanical measurement system can be eliminated. The 8450A Spectrophotometer achieves performance levels that are unattainable for conventional optomechanical systems. Integration of its electronics with its optomechanical system makes this performance possible without sacrificing low cost or producibility. Also, with its microcomputer and solid state memory, the 8450A can adapt dynamically to disturbances that otherwise would degrade system performance.

The electronics in the 8450A Spectrophotometer may be divided into three subsections: the input section, where incident light energy is translated to an electronic measure understandable to the microprocessor system, the beam director section, where the optical path is dynamically altered to serve multiple sample stations while guaranteeing photoreproducibility, and the microprocessor control and data system, where internal and external information is manipulated to produce answers immediately useful to the user. An overall block diagram of the electronics is shown in Fig. 1. The input system is described in this article. The beam director is described beginning on page 24, and the processor description begins on page 29.

Input System

Instead of using a single broadband photodetector that is mechanically scanned across the photo spectrum, the 8450A detects all elements of the spectrum simultaneously. Its photodetector consists of two silicon integrated circuits each containing 211 photosensitive diodes and 211 storage capacitors. The light to be detected is projected onto a bi-zone holographic dispersion grating that separates the light into its individual wavelength components. The reflections from the two halves of the grating are projected onto the photosensitive areas of the two detector arrays. Although each photodiode in the array is a broadband detector, its fixed position in relation to the dispersion grating defines the wavelength band of flux that strikes it. Thus the intensity signal for each photodiode may be treated as a data point in the frequency (wavelength) spectrum. 401 of these points make up an intensity-versus-wavelength spectrum of the incoming photo flux.

The photodiode array is an HP-manufactured PMOS* integrated circuit that is over ½ inch long. Each photosensitive diode in the array is 0.05 by 0.500 mm and has a spectral response that extends well beyond the 200-to-800-nm specification of the 8450A. An extensive research program yielded a proprietary process for eliminating degradation of the integrated circuit caused by long-term exposure to ultraviolet light. This in conjunction with extended temperature life tests results in an anticipated life greater than five years. A photomicrograph of the photodiode array chip is shown in Fig. 2.

A functional block diagram of the diode array chip is shown in Fig. 3. In parallel with each of the 211 photodiodes is a 10-picofarad storage capacitor. These diode-capacitor pairs are sequentially connected to a common output signal line through individual MOSFET* switches. When a FET switch is closed, the preamplifier connected to this signal line forces a potential of −5 volts onto the capacitor-diode pair. When the FET switch is opened again the current resulting from the light striking the photodiode causes the capacitor to discharge towards zero potential. A

*PMOS = P-channel metal-oxide-semiconductor.
MOSFET = metal-oxide-semiconductor field-effect transistor.
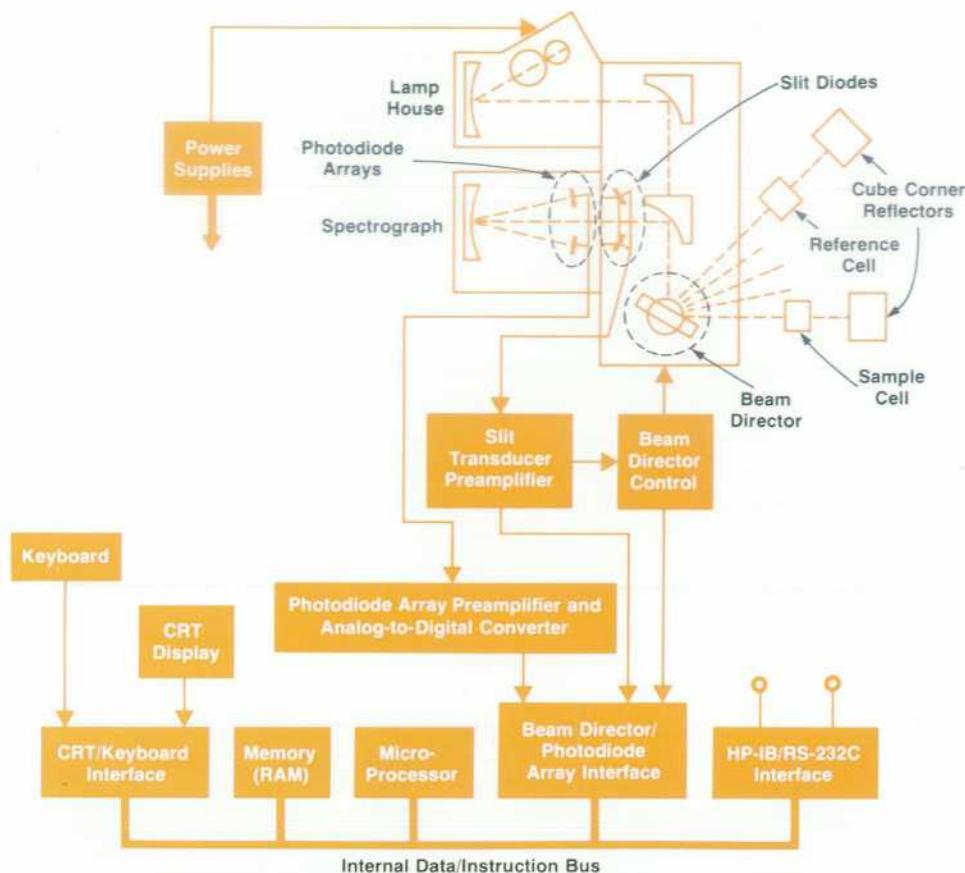
Fig. 1. *8450A Spectrophotometer electronic block diagram.*

measure of quality for systems like this is the degree of charge loss or leakage that occurs when there is no illumination. The diode arrays in the 8450A typically exhibit a leakage current less than 0.1 picoampere. This error term increases exponentially with temperature, but because the initial leakage value is so low, there is no need to cool the arrays to meet performance specifications at high ambient temperatures.
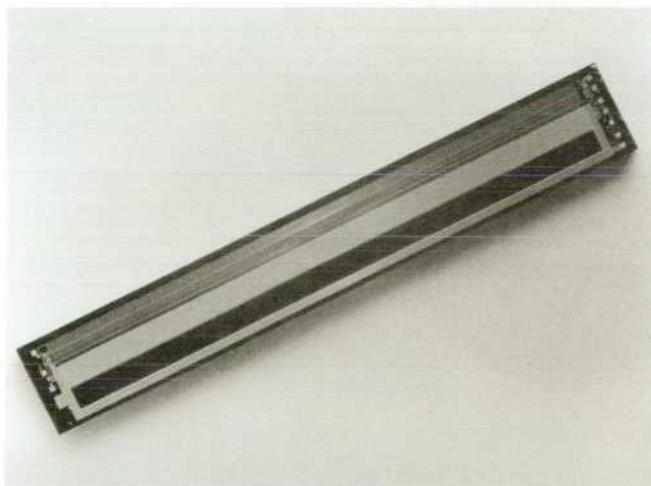
Fig. 2. *Photodiode array chip is a silicon integrated circuit containing 211 photosensitive diodes and 211 storage capacitors. Two of these chips are used to detect light at 401 wavelengths simultaneously.*

Serial readout of the diode array is accomplished by means of a digital shift register designed into the photodiode array chip. At the beginning of the output operation a logic one is applied to the data input of the register during the first transition of the clock lines. For all subsequent clock periods a logic zero is applied to this input. This causes the logic one to ripple its way through all 211 elements of the register enabling one diode-capacitor pair at a time.

The signal lines from both photodiodes arrays are tied to the input of the first amplifier, which is configured as a low-noise charge integrator (see Fig. 4). When a photodiode is connected to the array output line as part of the serial readout process, the voltage on that diode-capacitor pair is forced to -5 volts, and charge lost since this diode was last accessed is transferred to the integrator capacitor C_i. This results in a voltage proportional to light intensity at the output of the integrator stage. This voltage is stored by the sample-and-hold circuit and the integrator is reset, ready to access the next diode.

The output of the integrator is fed to the input of the programmable-gain amplifier, which attempts to scale the maximum response of each diode to the ADC input voltage range. This is necessary because the photocurrent generated in the diodes varies considerably over the spectrum, primarily because of variations in the output of the lamps, and efficient use of the ADC's resolution is necessary for meeting the baseline accuracy specifications. During the turn-on diagnostic, when the sample holders are clear of absorbers, the instrument finds and stores the highest gain
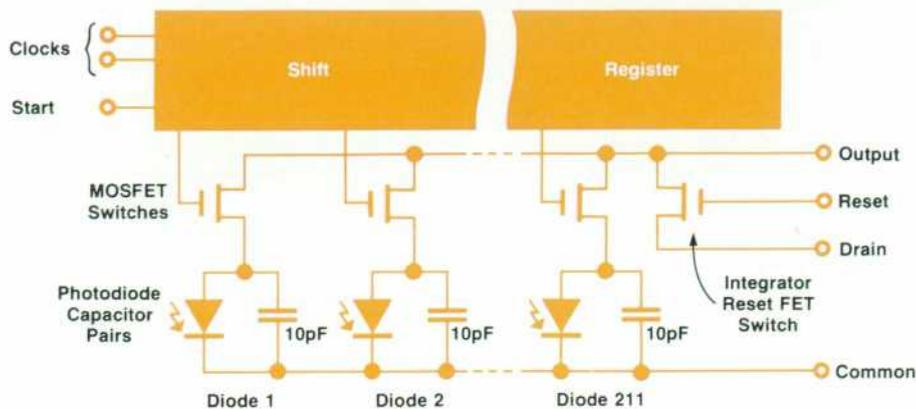
Fig. 3. Functional block diagram of the photodiode array chip.

setting commensurate with operation within the ADC's input range for each of the 422 diodes. During subsequent measurements the processor outputs the appropriate gain code for each diode as the serial readout proceeds.

Noise Compensation

During the reset operation of the integrator, the closed-loop bandwidth of the integrator amplifier is increased significantly. This increases the noise charge fluctuations at the inverting input node of the amplifier. These fluctuations are due to the input voltage noise of the amplifier. When the reset switch is opened, a "last" noise charge value is present on the inverting input node and this random charge appears in addition to the signal charge when the diode is being evaluated. Also, the thermal noise in the reset switch leaves a random noise charge on the integrator capacitor when the reset switch is opened. This charge also appears in addition to the signal charge at evaluation time.

The effects of both of these noise mechanisms are reduced by the analog subtraction circuit shown in Fig. 4. It consists of a series capacitor C_s and a switch that connects the output end of C_s to a fixed voltage. This switch is turned on just after the integrator reset operation, but before the next photodiode capacitor pair is connected to the integrator
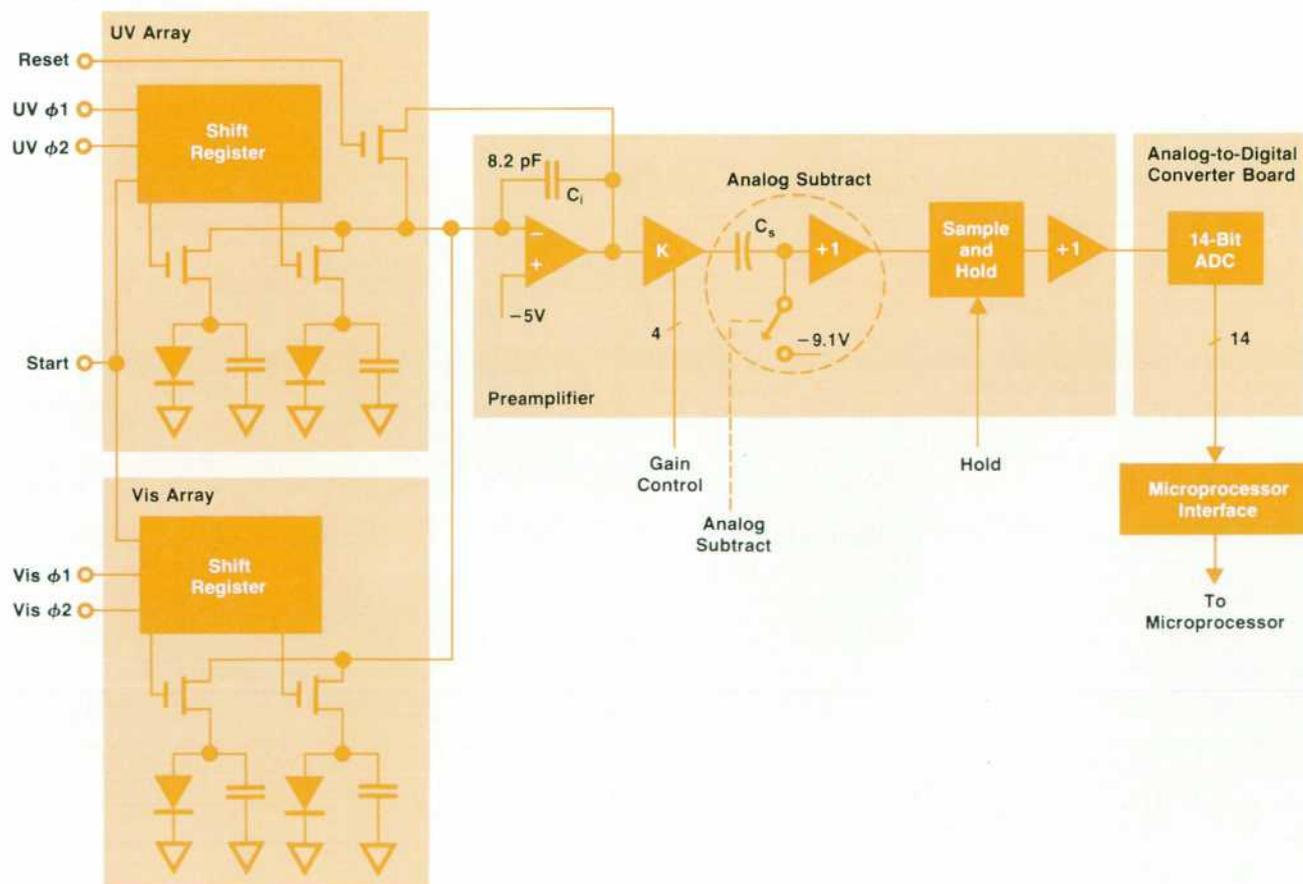
Fig. 4. Photodiode array readout system.

input. This causes the sum of the noise voltages from the two noise mechanisms to be stored on C_s, thereby subtracting this term from the output signal.

This technique introduces two other noise terms. First is the effect of the input noise voltage of the amplifier at the time the analog subtraction switch is opened. At this time the noise bandwidth of the integrator amplifier is much smaller and therefore the noise term is smaller than it was when the reset switch was opened. Second is the thermal noise in the analog subtraction switch, which is a much lower noise term than the integrator reset switch noise because C_s is significantly larger than C_i.

Analog-to-Digital Converter

The most expensive and critical single component in the signal path is the analog-to-digital converter (ADC). This converts the analog signals at the sample-and-hold stage into 14-bit digital words that are read by the microprocessor system. Since the ADC price seems to increase exponentially with the number of bits converted, careful analysis and experimentation were used to determine the necessary converter resolution. An extensive numerical modeling of noise mechanisms in the system pointed to a 12-bit conversion. An experiment using a very high-quality 14-bit converter produced the results in Fig. 5, which experimentally verify that ADC resolution beyond the 12-bit level will not enhance the overall system noise performance. To ensure adequate margin, a 13-bit converter resolution was deemed necessary, and a survey of commercially available ADC modules indicated that a 14-bit converter had to be purchased to guarantee 13-bit resolution over the operating temperature range of the instrument.

Since the basic measurement of the 8450A is a ratio of two measurements, each of which has had a noise floor subtracted, i.e., $(S-N)/(R-N)$, the requirements on the ADC are considerably eased. Any offset introduced by the ADC is cancelled mathematically. Similarly, geometric or gain errors cancel out of the above expression. Thus the only ADC error of significance is conversion nonlinearity. Nonlinearity was checked at the evaluation stage and is checked in production by a Corcoran, Hornak, Skov[1] method, as illustrated in Fig. 6. The computer in Fig. 6 outputs a series of 14-bit codes representing ADC code transitions to be measured. The measured code transitions are then compared to the theoretical locations of perfect code transitions and a plot of the resulting error is made on the X-Y plotter.

Each code transition is measured using the hardware

Fig. 5. *Experimental results showing that analog-to-digital converter resolution beyond 12 bits does not enhance overall system noise performance.*

configuration of Fig. 6. For example, suppose the computer puts out the binary representation of the number 5000. If the output of the ADC is less than or equal to 5000 the digital magnitude comparator forces an input to the analog integrator that causes its output to increase monotonically. When the output of the ADC reaches 5001 the input to the integrator reverses, causing the input voltage to the ADC to ramp downward. When the ADC output code reaches 5000 the ramp is again directed upwards. Thus a closed loop is created that causes the average voltage at the ADC input to represent the code transition between 5000 and 5001. This average input voltage is measured by an integrating voltmeter whose integration time is about 100 times greater than the ADC conversion time. Nearly 5000 points are checked and plotted to evaluate a high-quality ADC. Fortunately, an automatic test system can do this in less than 10 minutes. A plot for a defective ADC is shown in Fig. 7. Notice the differential nonlinearity present.

Fig. 6. *Analog-to-digital converter conversion nonlinearity test system.*
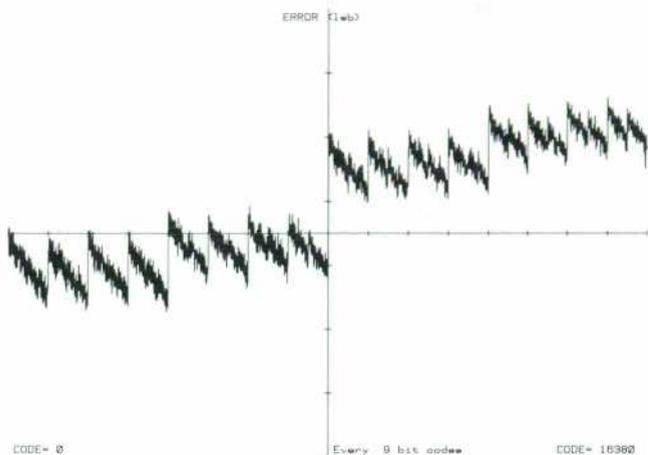
Fig. 7. *Conversion nonlinearity of a defective analog-to-digital converter measured by the system of Fig. 6. Nearly 5000 points are checked to evaluate an ADC.*

Resolution

The 8450A input section just described is a synchronous time-sampled current amplifier whose least significant bit of resolution represents 2.28 femtoamperes (2.28×10^{-15} A). Because this resolution is significantly less than the shot noise of the detection diodes, this noise can be digitized, so that several successive measurements can be averaged to further enhance system signal-to-noise ratio and provide statistical information about the measurements.

Reference

1. Corcoran, Hornak, and Skov, "A High-Resolution Error Plotter for Analog-to-Digital Converters," IEEE Transactions on Instrumentation and Measurement, Vol. IM-24, No.4, December 1975.

Knud L. Knudsen
An HP employee since 1963, Knud Knudsen contributed the electronic design of the low-noise input amplifier and signal processing system for the 8450A Spectrophotometer. He has also done device modeling and circuit simulation, and bipolar and MOS integrated circuit design. He is named inventor on three U.S. patents. Knud received the degree Electronic Engineer from the Aarhus Elektroteknikum in Denmark in 1957, and has taken further courses at the University of Santa Clara and Stanford University. Before coming to HP, he was with the Academy of Technical Sciences of the Royal Technical University in Copenhagen for six years. He's a member of the IEEE and of four IEEE professional groups. A resident of Los Altos Hills, California, Knud is married and has two children. In his spare time he enjoys tennis, skiing, and playing classical music on his Steinway grand piano.

Robert W. Widmayer
Bob Widmayer, a native Californian born in Hollywood, joined HP in 1975. He contributed the design of the input electronics and the ADC test system for the HP 8450A Spectrophotometer. Previously with HP's Disc Memory Division, he designed the motor power and servo control systems of the 7920 Disc Drive. Bob earned his BSEE degree from the University of California at Santa Barbara in 1975. He has been attending Stanford University part time and expects to receive his MSEE degree in June, 1980. Residents of San Jose, he and his wife own, train, and show their thoroughbred horse at California hunter-jumper shows.

Servo-Controlled Beam Director Provides Major Benefits

by Mark P. Morgenthaler and Lynn Weber

THE BEAM DIRECTOR in the 8450A Spectrophotometer is an unusual system component found in no other instrument. It solves many measurement and manufacturing problems and simultaneously provides major user conveniences. In retrospect, it is difficult to determine which of these factors was the main impetus in the evolution of this new component. It has, however, become such an integral part of the 8450A system that it is difficult to imagine how a spectrophotometer of this type could be built without it.
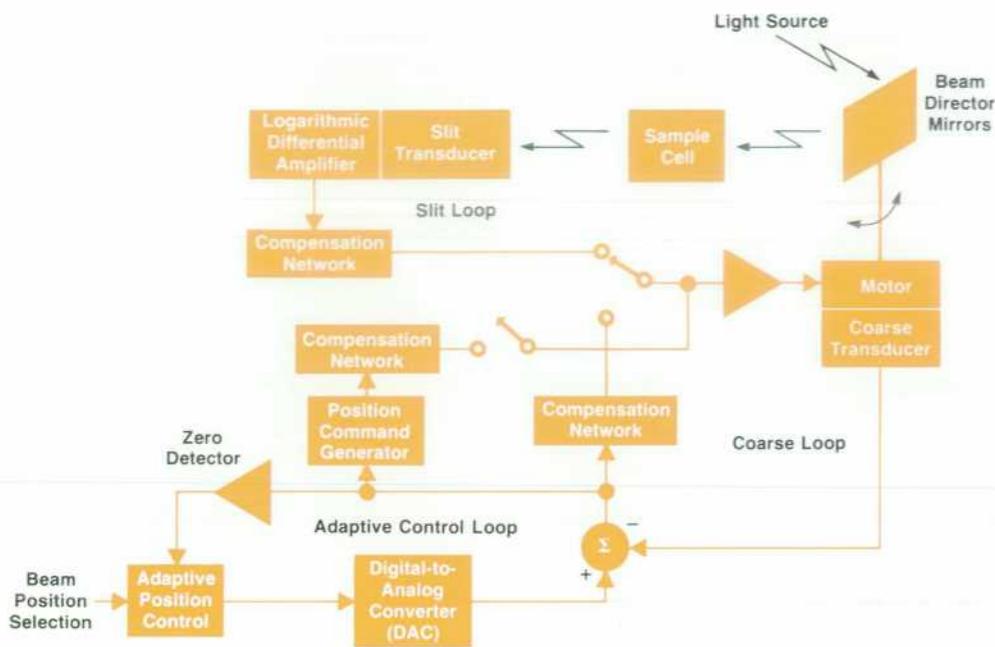
The beam director servo system performs the same function as the mechanically positioned chopper mirrors in a conventional spectrophotometer. In both systems, light is directed along two different optical paths by the movement of the mirrors. The two paths make it possible to measure the sample relative to a reference, thereby eliminating measurement errors caused by source instability. One reason for the beam director, therefore, is to provide a means for switching between optical paths.

The reason for selecting a servo system instead of a mechanical chopper system, however, comes from a more fundamental concern. In a conventional spectrophotometer, placement of the sample cell does not directly affect system performance. The beam from the light source is spectrally filtered before passing through the sample cell. Thus sample cell orientation does not affect the filtering process. Detection in the conventional system is usually done by a detector that has a relatively large aperture. With a large-aperture detector, variations introduced into the optical path by sample cell placement have little influence on the detected signal.

In the 8450A, however, optical filtering is done after the polychromatic beam has passed through the sample cell, and detection is accomplished by an array of small-area detectors. To assure accurate and repeatable wavelength calibration, the diodes, the grating, and the slit of the 8450A are mounted together in a single cast housing. This technique provides greater accuracy in wavelength calibration than is possible in a conventional system, but makes it necessary to assure that the beam incident on the spectrograph is aligned properly with the other optics in the instrument. In this type of system, small angular displacements of the sample cells will affect the optical path and disturb the detected intensity distribution and therefore the wavelength separation and detection functions.

Instead of requiring the user to work with an awkward high-tolerance sample cell mechanism to avoid angular displacements, the servo concept was devised. Thus, in a manner transparent to the user, angular variations occurring in the sample cell area are automatically corrected. This servomechanism is so sensitive that it can detect and correct variations in the optical path caused by refraction of the beam due to thermal gradients present in the air in a laboratory environment. In this new form of spectrophotometer, the beam director is a necessary component that assures proper registration of the beam on the detector slit and hence on the grating and detector diodes.

However, the beam director does more than provide a dynamically corrected optical path. Once the electronically controlled servo concept evolved, it was relatively easy to give the user the option of multiple sample cells with little additional expense. Also, manufacturing tolerances in other parts of the instrument were relaxed, since the servo corrects for certain misalignments. Thus the beam director has become an integral component of the 8450A, providing improvements in performance, manufacturability, and user convenience.

Design Concepts

Besides being interesting as a new system component, the beam director incorporates three novel design concepts. The first concept, the slit transducer in the slit servo loop, makes it possible to position the beam very accurately in the presence of large variations in light intensity without disturbing the loop gain. The second concept, the adaptive control for the coarse servo loop, provides precision control without expensive precision components.

The third concept, the position control system, provides near optimal control without a tachometer. The functions of these three elements are shown schematically in Fig. 1, the beam director system block diagram.

Optically the beam director consists of two precision flat front-surfaced mirrors mounted on a common shaft such that the mirror surfaces are coplanar and on the shaft axis (see Fig. 2). The shaft is rotated by an integral printed circuit brushless dc motor, which requires power only while mov-
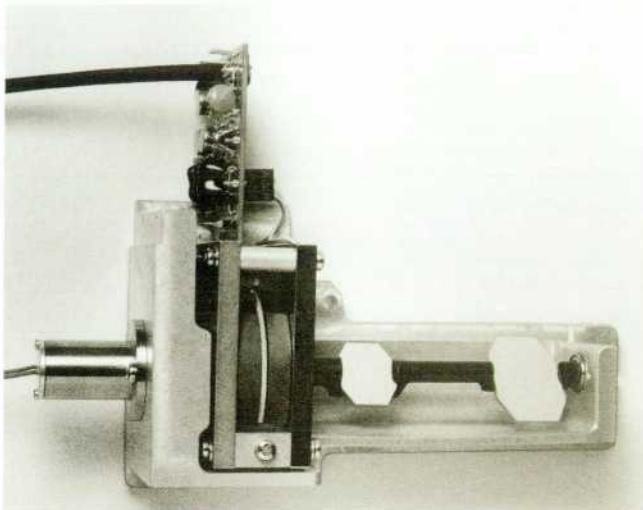
Fig. 2. *The two beam director mirrors are precision flat front-surfaced mirrors mounted on a common shaft. The shaft is rotated by a printed circuit brushless dc motor.*

ing. The stator is composed of four ceramic permanent magnets bonded to two steel plates. The rotor is fabricated as an eight-layer printed circuit board with a total of 64 turns. The beam director is positioned according to commands sent from the instrument's microcomputer.

The beam director is required to complete any movement of the beam in less than 146 milliseconds and to settle to within three seconds of arc of its final position in that time. Three arc-seconds of shaft rotation represents a lateral beam displacement of about 0.5 micrometre at the aperture of the 8450A detector.

Slit Servo Loop

Precise control of the beam position is the job of the slit loop shown in Fig. 1. To measure and correct for changes in the optical path, monitoring of the beam position after the beam has passed through the sample is mandatory. This necessarily results in a servo loop that is closed by an

optical path. The beam used to detect the optical path has to be the same beam that is used to make the photometric measurements, so the slit loop must be insensitive to the enormous spectral and intensity variations introduced by samples of various absorbances and compositions.

To accommodate these variations and achieve the required positioning accuracy, the slit servomechanism uses an unusual transducer that incorporates the spectrograph entrance slit (see Fig. 3). The slit transducer consists of a preamplifier and two large-area photodiodes located at the spectrograph slit. Each diode is mounted facing one of the spectrograph slit blades. The blade surfaces are polished and coated in the same way as the other optical surfaces in the instrument. Since the width of the beam is nominally twice the width of the slit at the spectrograph, approximately one-half the total measurement beam is reflected back to the two slit photodiodes. The slit preamplifier compares the outputs of the two photodiodes to determine the relative light levels on each side of the slit. It then outputs a signal that represents the position of the center of the beam relative to the center of the slit.

With this balancing form of detector, large common-mode changes in the optical spectrum can be tolerated. This type of detector always produces a proper balance regardless of spectral variations, but does cause the transducer transfer function to vary with light intensity. To avoid the resultant variations in loop gain, a logarithmic amplifier is used for each diode, and the outputs of the two amplifiers are subtracted, making the net output of the slit loop transducer proportional to the *ratio* rather than the difference of the light intensities on the two diodes. The transducer transfer function is not really linear, but over the small range of use that the system optics allow, the slope change is imperceptible. The output is therefore independent of total intensity. This type of transducer provides an extremely accurate position sensor capable of operating under variations in beam intensity and spectral composition of several orders of magnitude while maintaining nearly constant accuracy and system loop gain.
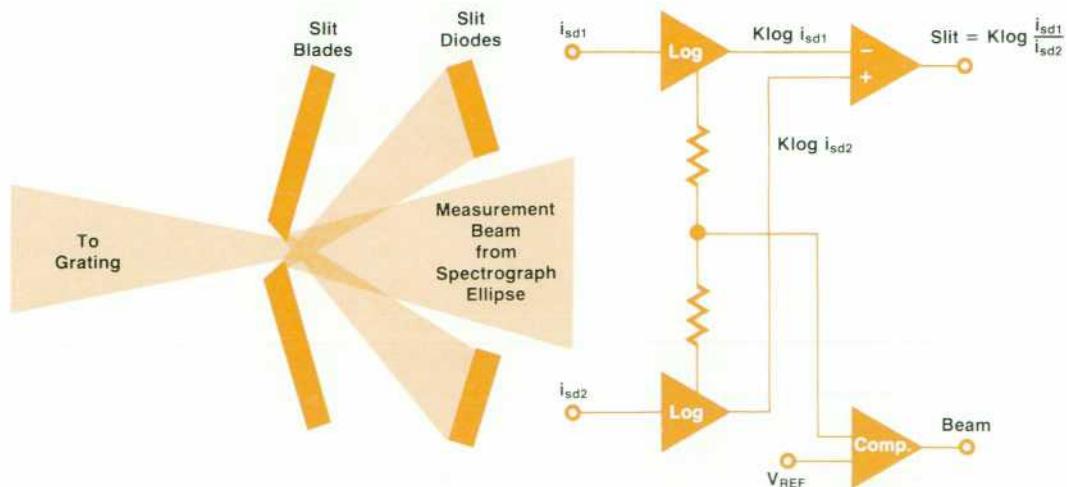
Fig. 3. *Slit loop transducer uses two photosensitive diodes to detect light reflected from the sides of the spectrograph entrance slit. To center the beam on the slit, the system balances the diode currents.*
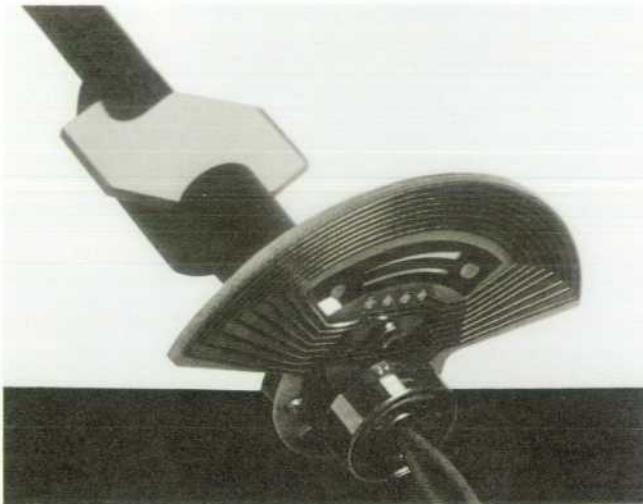
Fig. 4. *Two slots built into the motor that turns the mirror shaft are part of the coarse servo transducer.*

Coarse Servo and Adaptive Controller

The adaptive loop controller provides a means for decreasing the expense and increasing the reliability and serviceability of this servo system. To control beam movement over the entire sample cell area, a coarse loop transducer with a large angular range is used. The function of this transducer is to provide a means of control during movements between sample cell positions. Once a new position has been accessed, the slit transducer is used for final positioning of the beam, rather than the coarse loop transducer.

The slit detector transducer, as explained previously, is a precise indicator of position. However, it provides position information only over a very limited angular range. For the slit transducer to perform the final positioning, the coarse transducer must position the beam within the active range of the slit. This range is very small. The total sample space represents about 24 degrees of beam director shaft rotation, but the slit transducer is usable over only about three minutes of arc centered on the centerline of each measurement beam position.

Because the slit servo provides an absolute position reference, information is available to calibrate the coarse servo transducer continuously. The two servos, along with the instrument microcomputer, form an adaptive control system. This results in a considerable relaxation of the precision required of the coarse servo transducer.

The coarse servo uses a transducer built into the motor. This transducer consists of an LED (light-emitting diode) source mounted on the lower motor plate, a glass transducer window bonded over a hole in the rotor board, and two diode detectors with their associated circuitry (see Fig. 4). The glass window has two circumferential openings, one of constant width and one that tapers. The LED illuminates each detector diode through one of the openings. The beam director transducer circuit regulates the LED to a constant intensity as perceived by one of the detector diodes through the constant-width slot, and outputs a voltage proportional to the intensity of the LED as perceived by the other detector diode through the tapered slot. This output is proportional to the angular position of the tapered slot and hence the angular position of the shaft. The shape of the tapered slot is carefully chosen to linearize the transducer output.

The microcomputer positions the motor by sending digital addresses to the beam director system. These are converted to an analog signal by an eleven-bit digital-to-analog converter (DAC). This analog signal is then balanced by the coarse transducer output.

The digital address of the beam position is stored in an eleven-bit register. The three most significant bits, the coarse address, represent one of the five possible beam
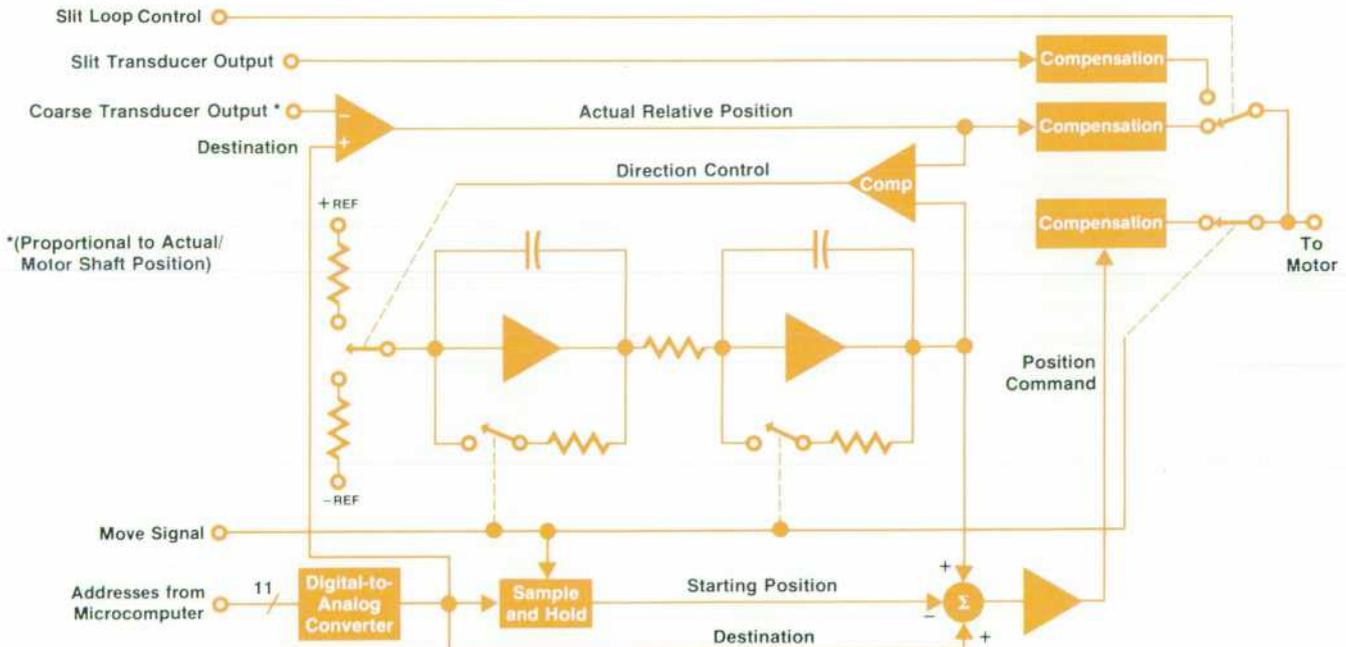
Fig. 5. *Beam director position command and control circuits.*

positions. The least significant eight bits, representing the fine address, are actually stored in an up-down counter. When the system is using the slit servo, the coarse servo loop is open, and the analog equivalent of the address is compared to the coarse transducer output. Any imbalance detected in this comparison causes the up-down counter to increment or decrement until the imbalance is corrected. The updated output of the address register is then stored in the microcomputer and used in subsequent moves.

In this way, the microcomputer monitors the position at which the beam actually settles and recalibrates the system continuously, while it is in use. Deviations from absolute stability and linearity can be compensated under processor control, thereby eliminating the need for highly stable, accurate and expensive components. In addition, because the microcomputer is an intimate part of the loop, information is available that aids diagnosis of actual and potential failure modes. This increases system reliability and serviceability.

The microcomputer is also used to implement a search algorithm that determines the active beam positions when the 8450A is first turned on. For each of the five possible beam addresses (one reference and four sample paths) the beam director is swept through the fine addresses until the slit preamplifier detects a signal at the slit diodes. The adaptive control system is then used to determine the most accurate address for each active beam position. This also eliminates production calibration for the beam addresses.

Position Command System

Several conflicting requirements influenced the design of the coarse servomechanism. Many similar electromechanical servos share the same performance-limiting characteristic—a maximum possible acceleration based on an input-current-limited magnetic structure. Maximum performance for such a servo, meaning that the time required for any movement is as short as possible, occurs when the system accelerates at the maximum rate for half the distance to be traveled and then decelerates at the maximum rate to the destination. This kind of control is typically achieved by generating the corresponding linear velocity ramps and forcing the moving structure's velocity to match these ramps by comparing the ramps in a servo loop to the output of a tachometer (velocity transducer) attached to the moving structure.

The 8450A beam director had little room for a tachometer. Therefore, the servomechanism was designed to control acceleration by following a position command waveform rather than a velocity command waveform. The position command is generated by two series integrators (see Fig. 5). The input to the first integrator is a constant current of either polarity that represents constant acceleration in either direction. The output of the first integrator is typically a triangular waveform that represents the velocity profile and the output of the second integrator is the desired position-versus-time waveform. The integrator time constants are just slightly longer than the time constant (the rigid body dynamic mode) of the moving structure. This leaves some current margin available to assure that control of the motor is maintained at all times.

The integrator output always starts at zero volts, but the desired position command must end at zero volts, indicating no difference between the desired position and the actual position. An initial offset is required that represents the displacement of the destination address from the starting address. A sample-and-hold circuit is used to store the output of the DAC for the starting address and then the DAC output for the destination address is subtracted to offset the integrator output.

The generated position command is used until the shaft gets to within about one minute of arc of its destination and then the servo is left to settle. If the move is to an address where the slit transducer detects a signal returning from the optical path the slit servo is then enabled and the motor and shaft are allowed to settle to the final position.

Lynn Weber

A native of Hollywood, California, Lynn Weber received his BSEE degree in 1968 and his MSEE degree in 1970 from the University of California at Berkeley. With HP since 1970, his projects have included the 5500C Laser Interferometer and accessories, the 7905A and 7920A Disc Memories and the 8450A Spectrophotometer. He's named inventor on two pending patents on the 8450A's beam director. Lynn is presently working in product support, helping to develop an 8450A service training course. His leisure time is taken up with his interest in flying (he's half owner of a Mooney), his salt water fish collection, and some amateur radio. Lynn and his wife and daughter live in Saratoga, California.

Mark P. Morgenthaler

Mark Morgenthaler came to HP in 1973 following his graduation from Stanford University with a BSEE degree. He received his MSEE in 1974, also from Stanford, and his JD law degree in 1978 from the University of San Francisco. Mark's contributions at HP Laboratories include work on a new oscilloscope design and the 8450A Spectrophotometer. He has served as project manager for several research projects. He is named inventor on a pending patent on a high-speed ADC. In addition to his engineering responsibilities at HP, Mark is the managing partner in a Palo Alto law firm and holds membership in the IEEE, the State Bar of California, the Santa Clara Bar Association, and the International Common Law Exchange Society. Active in the Neighborhood Improvement League in San Francisco, his hobbies include classic cars and the restoration of San Francisco Victorian houses. A native of Chicago, Illinois, Mark lives in Palo Alto, California.

A Microcomputer System for Spectrophotometric Data Processing

by Glenn C. Steiner

THE REQUIREMENTS of the high-speed, user-oriented 8450A Spectrophotometer made it mandatory that a powerful computer be built in to handle the large amount of data generated during spectrum measurements. The data had to be acquired, processed, and then handed to the operator in an understandable format. User interaction with the instrument had to be handled in such a manner as to make the 8450A a "friendly" machine. This powerful computer had to be reasonably priced and fit in a space not much larger than a breadbox.

Fig. 1 is the block diagram of the controller that was designed to meet these requirements.

SOS Processor

In a typical one-second measurement over 2000 data items are acquired for processing. At least 100 operations are applied to each item, giving 200,000 sixteen-bit operations that have to be done in less than a second. During the initial phases of the 8450A project, nothing short of a large minicomputer could process this much data. However, HP's state-of-the-art silicon-on-sapphire (SOS) process[1] came on-line during the project and produced a microprocessor system with the computing power of a minicomputer. The MC5 processor is an SOS part with TTL-compatible inputs and outputs. It can execute a typical instruction in about 1.5 microseconds.

The MC5 was designed as a fast microcontroller chip and does not have powerful arithmetic capabilities. Therefore, an external sixteen-bit multiplier was designed to handle the 20,000 multiplications required every second. This
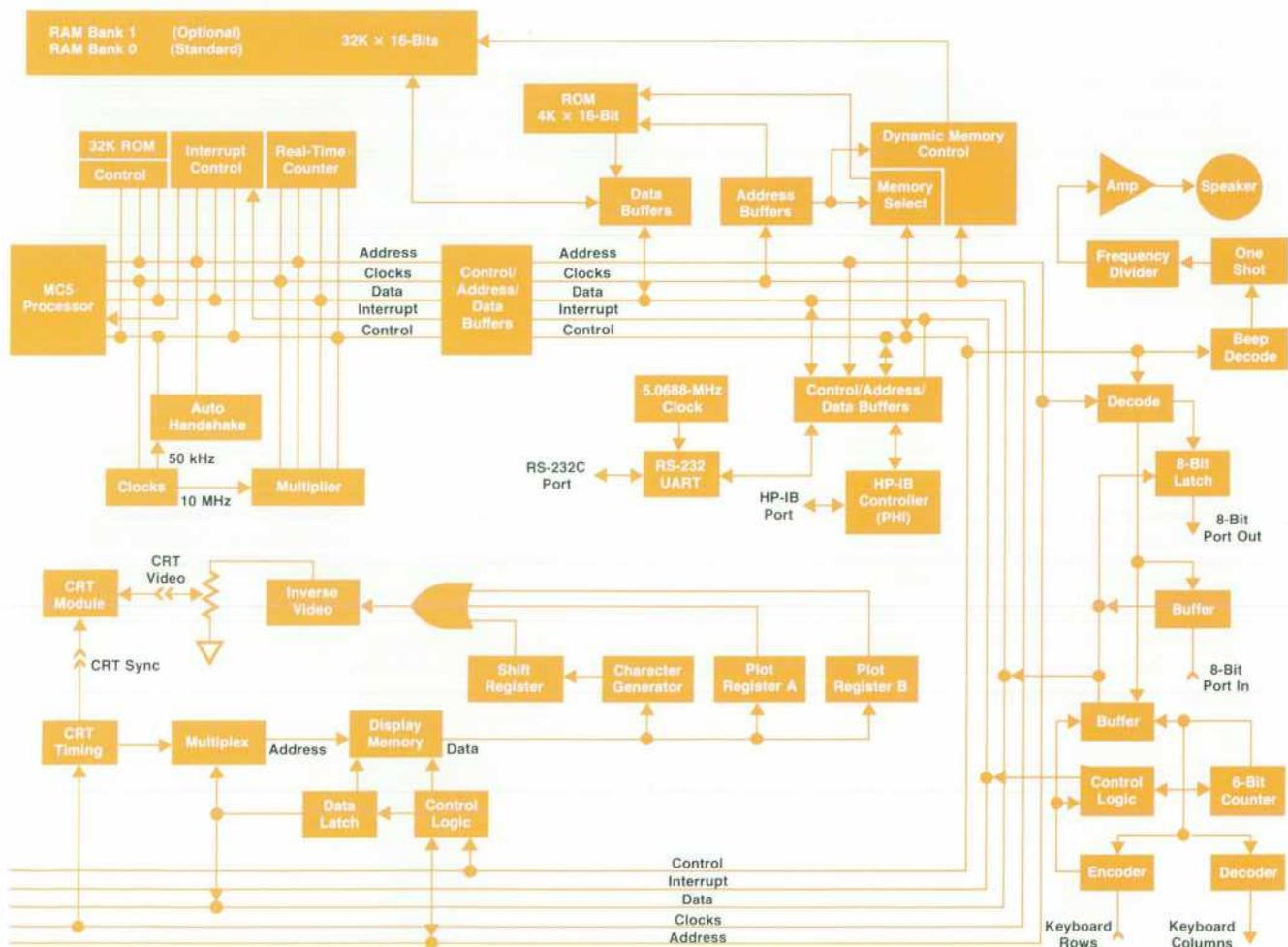
Fig. 1. Controller of the 8450A Spectrophotometer is a powerful computer that processes the large amount of data generated during measurements and presents results to the operator in an understandable form. It also makes the 8450A a "friendly" machine to operate.

multiplier can multiply two signed or unsigned sixteen-bit numbers and produce a 32-bit result in 1.6 microseconds. The multiplier is used for all multiplications, squaring, left shifts, and transcendental functions.

A large amount of preprogrammed code was required to give the 8450A its personality (see article, page 11). A total of 57,344 bytes of code is stored in 14 read-only memories (ROMs). To accommodate different manufacturers, the ROM support circuitry accepts ROMs from several different suppliers and allows ROM speeds to be intermixed.

To store the large amounts of data acquired during a spectral reading, the 8450A is supplied with 32,768 bytes of random-access memory (RAM), enough to store seven complete spectra. With the optional 32,768 additional bytes of RAM, twenty-five complete spectra many be stored. The need for a large, fast, low-cost RAM made for a very interesting design challenge. To keep the cost, volume, and power consumption to a minimum, 16K-bit dynamic memories were chosen. However, dynamic memories require refreshing, multiplexing of addresses, and arbitration of refresh and processor accesses to the RAM. What had to be designed was a "black box" between the processor and the RAM. The box had to refresh the RAMs so data would not be lost, while allowing the processor to access the RAMs without having to wait for the completion of a refresh operation. Of course, the cost of the control circuitry had to be kept to a minimum. To solve all these problems, a synchronous state-machine controller was designed. A bipolar PROM (programmable read-only memory) is used to control the status of the black box and its outputs (Fig. 2). Latches and a 20-MHz clock maintain outputs and synchronize the logic. The result is a low-cost dynamic memory controller that allows fast access to the RAMs with hidden refresh operations.

Input/Output Interfaces

In any data acquisition system it is important to have a means by which data can be recorded on a mass storage
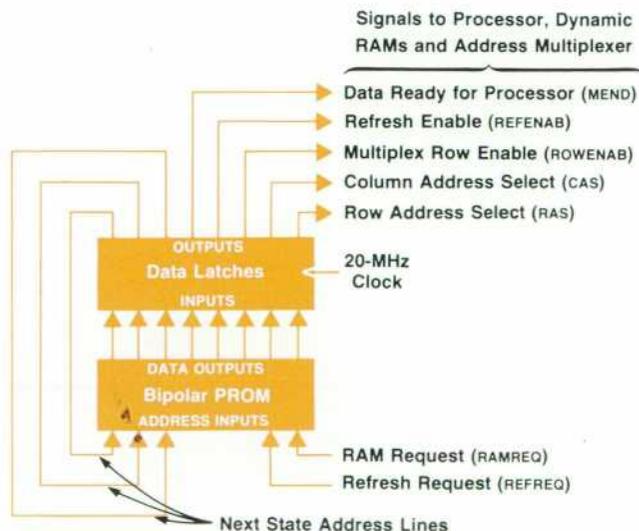
Fig. 2. *Dynamic memory controller is a synchronous state machine that refreshes the dynamic memories while allowing the processor to access the memories without delay.*
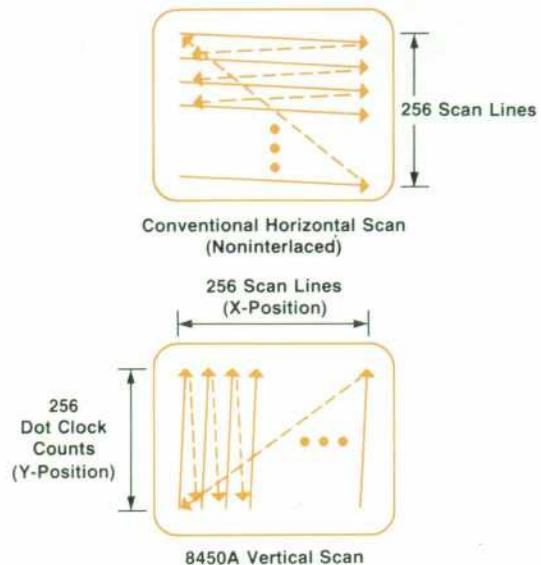
Fig. 3. *The 8450A's CRT scans vertically instead of horizontally as do most raster-scan CRTs.*

device for later use or on a hardcopy device for human inspection. Other input/output operations that were desired for the 8450A included: communication with other serial devices, relay control of valves, pumps, and samplers, and remote control by a desktop computer or larger computer. To achieve these goals, two industry-standard communications interfaces were included in the 8450A. The first, a serial RS-232C interface, allows data and programs to be sent back and forth beween the spectrophotometer and many common modems and computers. The information may also be sent to standard RS-232C-compatible printers for data and program documentation.

The second interface is the HP-IB. This bit-parallel interface is Hewlett-Packard's implementation of the IEEE 488-1978 communications standard. Through the HP-IB one may easily record and retrieve data and methods on the HP 9875A Cartridge Tape Unit. Measured or calculated results may be neatly plotted or printed and labeled on any of three different HP plotters. An HP-IB printer may be used to print the results. HP's SOS process has also made it possible to design a powerful HP-IB controller chip, the PHI.[2] This part contains over 8000 transistors. It allowed us to design an HP-IB interface with five integrated circuits, whereas previous designs required up to sixty chips. As a smart controller, the PHI also helps reduce the work required of the MC5 processor when communication is done over the HP-IB.

User Interface

The ways in which a person would interact with the 8450A were thought out with user convenience in mind. For input, a functional keyboard was chosen over the standard typewriter format. This was done to aid the operator in command selection. A flat, sealed keyboard was chosen for its resistance to spilled chemicals. To reduce the processor workload, external circuits were provided to scan the keyboard and interrupt the processor when a keystroke is detected. A speaker provides audible feedback with clicks for each keystroke and beeps for error conditions.

A five-inch-diagonal CRT was chosen over a single-line display or printer. The CRT can display up to 16 lines of 32 characters each and two plots of 256 points each. This display gives the user an easy and fast means by which results can be displayed, formatted, redisplayed and then plotted or printed. The days of lost peaks on plots because of poor scaling choices are gone forever.

The CRT used in the 8450A is unusual in that it scans vertically instead of using the conventional horizontal scan (Fig. 3). This scheme was chosen to aid in the display of plots. During a single display there are 256 vertical scans of the electron beam, with each scan broken into 256 dot positions. Two 256-by-8-bit RAM locations are set aside for plot data. When a point is to be plotted, its X value is used to locate RAM location X and its Y value is placed in that location. Later, when the CRT is doing a vertical scan in column X, the Y value in RAM location X is retrieved. This Y value is compared to the dot clock count, and when they match a point is displayed. This is a very cost-effective solution compared to systems that have a RAM location for every point on the screen (requires 8K bytes) or those that use costly associative memories.

Reliability and Service

For reliability, many unseen features are implemented in the processing system design. A TTL sixteen-bit microprocessor bus was defined for communication between boards. To reduce failures caused by static discharge, all CMOS parts are buffered from the bus by TTL gates. Boards are designed to place not more than two low-power Schottky loads on bus lines. Thus gates are never loaded above fifty percent of capacity. All external signals flow through the motherboard to the processing system boards. This greatly reduces stress on ribbon connectors and enhances reliability. Alignment pins at the motherboard prevent cards from being installed in the wrong slots or backwards. Finally, during the design phases, all boards are tested for reliable operation from -10 to $+80°C$, a range
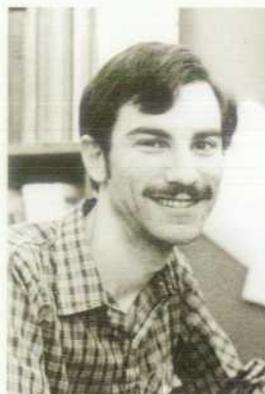
Glenn C. Steiner
Glenn Steiner joined HP in 1977 to design the microprocessor system for the 8450A Spectrophotometer. Born in Santa Monica, California, he holds BS and MS degrees in electrical engineering and computer science from the University of California at Santa Barbara and Berkeley, respectively. He's a member of the IEEE and the IEEE Computer Society, and lives in Palo Alto, California. Glenn's favorite pastime is dancing, be it folk, square, or ballroom. He's also putting together a home computer system and enjoys photography and skiing.

much wider than the instrument's specification.

To verify proper system operation and to aid service personnel in locating problems, a series of diagnostics were included to verify hardware operation. They are run at turn-on. First core parts are tested, and then the core is expanded and tested. Diagnostics start with testing the MC5 processor and expand by testing the ROM, RAM, multiplier, I/O, lamps, beam director, and finally the diode arrays and analog electronics. Once the 8450A is on, any of these diagnostics may be run individually, and other more comprehensive tests not done at turn-on, such as CRT or keyboard diagnostics, may be run. These tests locate a problem to a single board and greatly reduce the time spent in locating a problem.

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How the Model 8450A Was Developed

by Richard E. Monnier

UV/Vis R&D Manager

Some of our best products are developed when an existing need can suddenly be filled because of developing technologies. This is particularly true when a combination of developing technologies can be brought together, each making the other more useful in the new product. Much of the contribution in the new 8450 Spectrophotometer design relates to the way the developing technologies of holographic diffraction gratings, aspheric replicated optics, diode array photodetectors, and microprocessor control systems could be blended into a product to fill a need in a way not before possible.

Although relatively obvious now, the path was not clear along the way, especially in the beginning. The work on the spectrophotometer was started in Hewlett-Packard Laboratories. Barry Willis had joined HP hoping to help develop a capability in optical methods of measurement. Barry deserves special mention here because his expertise, enthusiasm, and persistence have contributed immeasurably to the whole effort from beginning to end.

Much of the early work in HP Laboratories was exploratory. During these first years many

possible ideas and alternatives were explored and many abandoned. The effort grew as new ideas held promise, and new people with a particular expertise became temporarily involved. Then the effort would, for some people, become part-time again. There were many who contributed during this time, too many to give proper credit to all.

The effort began with a proposal for the basic optical and performance concepts by Barry Willis and by Bob Chaney, who had the early management reponsibility for the project. Doug Smith worked on the early attempts to get a satisfactory diode array detector. Mike Kelly participated in the early investigation of alternatives.

The investigatory effort really started to be seriously pursued when a key element, an aberration-corrected holographic grating, became available. Conventional gratings had too much stray-light, ghost imagery, and aberration for use in the kind of spectrograph required for a system with array detectors. The optics design was spearheaded by Chuck Bryson, who contributed in most optical areas but particularly in the design of the spectrograph that is so

critical to the overall performance of the system. Fred Schwartz contributed to the design of the overall optics and the illumination optics. It was Fred who recognized the advantages of a confocal ellipse system and developed it for use in the 8450A. John Dukes contributed to the optical system in developing the beam director positioning concepts and in recognizing the role of the cube corners in a practical beam director system.

As the work started coming together in the form of a first breadboard system, the effort demonstrated progress and many more people became involved. A good deal of work was necessary in the detector system. Knud Knudsen was responsible for the electronic design of the low-noise input amplifier and signal processing system. Bill Mordan, Hap Horn and Bud Cristal contributed for a time in this area as well. Arpad Barna helped with a number of theoretical investigations of problem areas, since there were many fundamental design considerations during this period.

The first breadboard was a good start, but a new breadboard was needed to incorporate new ideas and more of the overall system. Bruce Ruff joined the optics effort to help with the optical component selection and evaluation of the optical performance of the system. Mark Morgenthaler did further development of the beam director concept and designed the related circuitry for the second breadboard.

The concepts that define the operation of the microcomputer are incorporated in the firmware operating system. This whole area was explored, debated, and defined by a fortunate combination of talented chemists and software people. As the system was designed it was programmed in a computer/disc system that simulated the microcomputer and was used to operate the second breadboard. Kathy Potter contributed significantly to the system through her software expertise and in writing the PARSER routine. Norton Bell, with his software background and logical approach, helped Kathy discipline the chemists and wrote the XCUTER routine as well as much more later on in the development effort. Paul Dryden helped with the chemistry and wrote the EXEC and MEASURE routines.

Art Schleifer, who helped the others see the system through the eyes of the chemist/user, wrote I/O routines and helped with the evaluation and selection of peripherals. Ray Bell, also a chemist, wrote the output format routines and methods, and eventually assumed responsibility for those portions written earlier by Kathy and Paul. Barry Willis contributed many of the concepts and tied the whole software/applications effort together.

The microcomputer was defined during this period with the guidance of Avner Ben Dor. Related was the work done by Andrew Stefanski on the fast multiplier to achieve adequate computational speed. Andrew also was responsible for work on the multicomponent analysis and for the CRT display. John Lazier helped immeasurably in the building of the breadboard and the design of all the little pieces necessary to put together a working system. Mike Farrell designed and built the keyboard and power supplies.

The mechanical design of the spectrophotometer was a major effort. Clarence Studley did much of the tolerance analysis and the mechanical design of the system and some of the optical parts such as the cube corners. George Drennan designed the mechanical parts of the beam director, the diode array package, and the slits. Jim Haynes designed some of the test fixtures and mechanical aspects of the sample area. Bob Hirsch joined the project for a short time to help with the mechanical design as well as tooling and manufacturing concepts.

It had earlier become clear that a major contribution had to be made in the diode array detector. Low noise, stability, and sensitivity had to be markedly better if a practical system was to be achieved. The Integrated Circuit Laboratory of HP laboratories was ready to help. There have been many people in ICL involved in this successful effort. Ted Kamins was responsible for the array design and process development, assisted by Godfrey Fong. Dancy Girot did the array layout.

The project went through a major transition when, basic feasibility demonstrated, the majority of the development effort was transferred to the Scientific Instruments Division. Some of the HP Laboratories people went on to different tasks, some continued to work in related investigations, and some transferred with the project. Some of the above mentioned people were SID development people who were temporarily assigned to HPL and moved back with the transfer to provide good continuity. Two such mechanical engineers were Bob Nordman and Gene Wong. Bob has done an extraordinary job in the mechanical design of many of the optical structures such as the spectrograph, the lamphouse, and the basic mechanical/optical structure of the system. Gene Wong has done most of the work on the mechanical packaging and has been heavily involved in the transfer to production.

In the two years since the transfer the development effort has gone through the normal HP product development cycle of lab prototypes, production prototypes, pilot run, environmental and reliability testing, and finally the transfer to manufacturing. During this period the project responsibility for the chemistry/firmware/optics has been ably handled by Barry Willis. Herb Stickel joined the group to take project responsibility for the mechanical and electrical design. Herb did a fine job of focusing the product development effort and brought his long experience in making a successful transition from the R&D lab to production. George Hopkins joined the project to take on the responsibility for completing the optics design. His careful analysis of the system and contributions to the optics design and development have been major factors in achieving a high-performance and producible optical system. Harry Wu also joined the project after it was transferred to SID. He has made important contributions in optical components and in the evaluation of the 8450A in new applications such as semiconductor processing.

Lynn Weber did further development work on the beam director electronics, designed the power supplies, and developed the overall electrical architecture of the system. Glenn Steiner accomplished the major task of completing the design of the microcomputer including the microprocessor, memory, multiplier, and input/output. Bob Widmayer completed the design work on all the signal processing circuitry and got all the component parts of the signal processing system working together properly. He also took over work on the CRT display and keyboard, which was handled for a short time by Jim Maples. Joel Harrison did a computer study of the vibrational properties of the beam director shaft.

A very important part of the design of any HP product is the industrial design. The requirements of the spectrophotometer were unusual and the special demands imposed by operating reliably and conveniently in the harsh environment typical of chemical applications and laboratories dictated a new cabinet design. It would operate with and alongside a variety of other HP products. Al Inhelder's corporate industrial design group contributed all along the way. During the HPL period Ed Salter consulted on on the early designs. Following the transfer to SID Ted Renteria did the industrial design so evident in the final product and many of the accessory items.

As the product approached production a whole new host of people became involved and contributed. I can only name some: Dave Gunn in the model shop, Gladys Klick and Marge Dodd in printed circuit design, Chet Haibel and John Ertel in production engineering, Bill Kruse in cost accounting, Stu Hanson on the operating manual, Alice Dooley in purchasing, and Marty Holderness in service. Frank Bunya, Larry Thompson and Jerry Rector helped with the successful transfer to manufacturing. Lynda Ratcliff helped prepare a mountain of documentation including this Journal.

Finally, some mention of the management attention this program received is in order. To us on the project it seemed that we had the eye and interest of a good many corporate managers. Their inputs and questions helped considerably in shaping this product into the fine technical and measurement contribution that it is. Special mention should go to Barney Oliver and to Paul Stoft for their patience and vision during those early uncertain years, and to Ivan Crockett for getting the program out of the investigative phase and moving toward the development of a real product.

The 8450A Spectophotometer happened because of the contributions of a large number of people. The result is a very significant step forward in chemical measurement capability and the excitement we have felt about what the 8450A can do is now visible in those who have had the opportunity to use it.

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