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Computer-assisted Spectroscopy

Abstract: The logical and timing requirements and the control circuitry of spectrometers in all energy ranges, chromatographs, scanning interferometers and microdensitometers, and a large class of related experimental apparati are very similar. From the standpoint of on-line computation and control, they can be considered parametric variations of a single experiment. With a magnetic resonance spectrometer as an example, we describe briefly the central, common elements of the necessary computer-instrument interface and of adequately flexible and open-ended control programs. Some examples of results follow.

Introduction

Although there has been widespread discussion of computer-assisted experimentation in recent years, with a few isolated exceptions the promise of presently available technology has not been realized in physical or analytical chemistry laboratories. Most of the relevant literature seems to deal either with elements of technique (either instrumental or logical) applicable to a range of experiments or with particular experiments in conjunction with particular computers. Many of the experiments under consideration exhibit more similarities to each other than differences, when one considers them as controlled data-gathering tools; moreover, their logical requirements are a great deal simpler than is generally considered to be the case. The purpose of this paper is to use these elements of similarity as the basis for a discussion of computer-assisted experimentation from a chemist's point of view. We particularly wish to show that, even for a research tool requiring great flexibility,[1] the interfacing hardware can be quite simple, does not require any special techniques, and need not impeach the "stand-alone" capability of the laboratory instrument. Also, with modular logic and appropriate high-level subroutines, the associated user's programs can be as flexible as necessary, without requiring as complex a programming effort as might be anticipated.[2]

In this laboratory four instruments are presently "on-line" to an IBM 1800 process control computer. These are a paramagnetic resonance spectrometer, a single-beam optical absorption spectrometer, a vacuum uv reflectance spectrometer and a vapor-phase chromatograph. Most of the comments of this paper are applicable to any of these instruments and to others we are presently connecting. For explicitness in illustration, the interfacing hardware and programs for the paramagnetic resonance are described in detail. Since it was the first experiment "on-line" here, it is serving as a prototype for some of the other experiments.

Recently we examined the computational requirements of spectrometers and similar instruments, and found that they were simple enough for it to be an easy task to provide flexible time-shared data-logging and control of multiple experiments.[3] The present paper is restricted as much as possible to ideas and techniques applicable either to time-shared or dedicated computers. However, the system in use in this laboratory is a time-shared one, so that some features which are necessary to avoid interference and undue delay between experiments and which are, therefore, possibly unnecessary in dedicated systems, do enter our description.

It is profitable to classify those chemical instruments currently under consideration for on-line computation into three categories: (1) those which require some computation after each data transfer between the instrument and a computer, e.g., x-ray diffraction of single crystals; (2) those which scan moderately quickly (kilocycles/sec) e.g., residual gas analyzers; and (3) those which scan quite slowly. We have chosen to deal explicitly with the requirements of the third class, since it is at once the simplest class and the most common[4] and since its requirements can be shown to be compatible with those experiments of the first two classes without serious conflict on the same time-shared computer. Following a delineation of the relevant common numerical control and physical charac-

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teristics of slow-scanning spectrometers, we describe the electrical interface and, with simplified flow charts, the programs for an electron paramagnetic resonance spectrometer.

On the common features of spectrometers[5]

A spectroscopic experiment is performed to find the functional dependence of some dependent variable(s) on some independent variable(s). Generally the independent variable is varied monotonically in time although it has been suggested that various sources of low-frequency noise could be eliminated by pseudorandom variation of the independent variable. Often one or more parameters, e.g. temperature, will be held constant during portions of the experiment and then advanced to new values. Although the controlled variables are swept in real time, there is no unavoidable reason why sampling intervals must be controlled accurately; for those experiments for which time or some other uncontrolled parameter is the independent variable it is generally adequate to record the intervals rather than control them.[6] The data need not be interpreted during the course of a scan but may be processed after the collection cycle is completed.[7] Analog integration to improve signal-to-noise ratio is a common feature of spectroscopy; it introduces a natural time constant, characteristic of the experiment and typically in the range 0.1 to 10 sec. Fast sampling has no intrinsic advantage for experiments which necessarily involve an integrating output.

A spectrometer may be considered the aggregation of three units: a device for the control and production of the independent variable, a device to sense, amplify and integrate the response of the sample, and a set of devices to control and apply to the sample such auxiliary stimuli (temperature, orientation, etc.) as may be appropriate. In each case, the computer interface must be added to the control circuitry for the transducers. Although the transducers differ on various types of spectrometers, the control circuits are remarkably similar; this is particularly true of detection circuitry. The majority of spectrometers have phase-sensitive detectors[8] that include most of the signal controls which are worth interfacing. Perhaps it is worth mentioning that quite commonly the most stringent precision requirement of a spectrometer is associated with the independent variable, so that a digital signal seems necessary for it in each of our experiments, whereas we find it most convenient to transmit our outputs to the computer as voltages.

Control of the independent variables changes somewhat from experiment to experiment. Presently we recommend that such controls be designed as the simplest method of modifying existing circuits. One example (for magnetic field control) is given as an appendix. For a number of applications in which shaft positioning is involved (grating spectrometers, microdensitometers), a simple stepping-motor circuit has been devised in this laboratory.[9] But although there are variations in these circuits, the number and purpose of the signals which should be interfaced to a computer change little from instrument to instrument. They should include all those controls and signals which are frequently modified during the course of an experiment. Typically they include digital control of the swept variable, analog sensing of the detector output, digital control of the gain and time constant of the detector controls for "parameters," and a pair of analog outputs for laboratory presentation of graphical results on an *x-y* plotter or storage oscilloscope. A typewriter in the laboratory is invaluable. The hardware interface between a spectrometer and a computer can be designed with very little reference to the programs with which it will be associated.

Communications between an experiment and a computer are either one-of-a-kind accesses, such as resetting a gain control, or repetitive tasks which can be executed in a background mode, since they require a very low computer duty cycle. In the programming system used in this laboratory, the former are implemented by FORTRAN calls from foreground programs to the subroutines which control the process input/output terminals of the computer. The repetitive, time communications are accomplished by the set of monitor subprograms previously described.[3] Any program may request background service from the monitor program by a call to a subprogram called INIO in the previous paper. INIO initiates, for a specified number of steps with specified timing, data transfers between the computer and the experiment. The possible operations at each step include digital and analog input and output commands of several types, which can be combined appropriately for the experiment in question. The reader is referred to the prior publication[3] for details. This routine has enough flexibility for all of the experiments that we have interfaced to date. Extensions to some anticipated situations and improvements in efficiency are planned in the near future.

A particular spectrometer

The particular instrument[10] used as an illustration in this article is a custom-built X-band superheterodyne electron paramagnetic resonance (EPR) spectrometer primarily used for the study of transition metal impurities in single crystals at low temperatures. Our first objectives in interfacing this experiment to a process-control computer were to accomplish the initial tedious search for a signal automatically and with better documentation than had been maintained in the past; to provide accurately calibrated plots of spectra as a function of orientation of the magnetic field in the sample; to have the computer locate lines in the presence of noise and tabulate their positions for input to programs giving least-squares analyses to fit

spin Hamiltonians; to improve the quality of the data by the well-known computer-of-average-transients operation;[11] and to accomplish certain simple filtering tasks such as smoothing and improvement of spectral resolution. Since scans are quite slow (typical duration is 15 minutes), leading to experiments that continue for days, and since we could not define clear objectives for a possible man-machine link, we chose an organization in which an initial set of commands controls a long series of experiments, with certain rudimentary feedbacks as a consequence of the data collected and with the possibility of manual intervention in the command sequence at a number of logical check-points. The entire command sequence is readily altered.

• *Hardware interface*

For the paramagnetic resonance spectrometer the interface includes digital control of the magnetic field (which is the independent variable usually swept), analog sensing of the output phase-sensitive detector, digital control of the gain, time constant and modulation amplitude, a positioning mechanism for the 12-inch rotating electromagnet, and analog outputs to an x–y recorder in the laboratory. All these functions are accomplished with two digital output words (16 bits each), two analog output voltages and two analog input voltages. Most of the other controls of this spectrometer are used only at setup time and were not interfaced to the computer. (In addition to the above connections, we are using two low-priority interrupt lines to provide certain restart capabilities and a number of test functions[12] and a single digital input word (also 16 bits) to allow experimenter limited communication to the computer during the experiment by means of panel toggle switches.) Details of control of the magnetic field amplitude and direction are peculiar to magnetic resonance spectroscopy and are therefore relegated to an appendix.

Control of the time constant, gain and modulation amplitude in the phase-sensitive detector is achieved with conventional addressing trees of reed relays driven by one digital output word. To these functions are assigned respectively 2 bits, 4 bits, and 4 bits of the output word. Since an n-bit set has 2^n states, the computer can command four values of the time constant, chosen to be 0.3, 1, 3, and 10 seconds. For the gain or the modulation amplitude, the computer can set 16 values, chosen to range over four orders of magnitude. The only modification to the existing phase-sensitive detector was the addition of addressing circuits in parallel to the corresponding panel controls, with local-remote relays choosing which circuit would be active. We have a program capability of setting any subset of bits of a digital output word without affecting the other bits, so that independent program instructions may be used to control these independent parameters. The same digital output group also controls the magnet rotation motor (1 bit), the penlift (1 bit), and event marker (1 bit) on the local x-y recorder and the allocation, under program control, of the analog lines to various functions, e.g., one digital-to-analog converter services either the ordinate of the x-y recorder or the reference terminals of the magnet's position sensing potentiometer. We believe that about one digital output word (16 bits) is sufficient for all such controls in any spectroscopy experiment. Both digital and analog signals are carried to the computer 250 feet away on twisted pair conductors. For the analog signals it is easy to arrange signal levels of 0.5 volt or higher and appropriate filtering at the computer, so that the noise pickup on the cable is negligible.[13] While a spectrum is being recorded, the x-y recorder is switched to monitor the input to the computer, with the x-axis sweep provided by the computer. Between sweeps it is connected to the computer as an output medium.

• *Programs*

The user's programs associated with the paramagnetic resonance experiment have been described previously[3] in a cursory fashion. In the present paper we would like to discuss in somewhat more detail the criteria for the design of such user's programs and an organization for them using the EPR system as an example.

The "EPR Observation" program design is predicated upon the assumption that, in a research environment, it is neither desirable nor always possible to predict the order of a series of operations or their timing. As our experience with computer-assisted spectroscopy increases we anticipate that the operation repertory will expand. Therefore, a user's program should be open-ended with respect to the number and type of operations allowed and permit these operations to be carried out in any reasonable order. It should be capable of executing a long command string without operator intervention or, alternatively, allow the experimenter to intervene and exert personal control. It must either process each spectrum before the next is collected, or provide for storage and cataloging of large numbers of data sets.

We have chosen to process each set of scans shortly after their collection. If the monitor system under which the program operates does not provide any arithmetic facilities during the time a spectrum is being collected, it must be organized into scan and data-processing phases. The ability of our monitor in this laboratory to accomplish data-acquisition and delayed-control functions in a "background" mode has been exploited to make efficient time-shared use of the central processing unit and main memory of the computer, and to relieve the user of any tricky interface programming. Partly to make it possible to release control of the computer during data-collection phases and partly to facilitate programming operation modules independently of each other, the programs are built around

the use of disk files both for command data and object data. The control file contains a counter indicating the current task being executed and a list of integer task identifiers with indications of the location of whatever auxiliary data are required for each task. There are two associated data areas on disk, one in integer format for the current spectrum being recorded and the other in floating point format for "catting" and all the data-processing tasks. With the assumption that object data were not available in core memory but only from disk storage, each module in Fig. 1 could be programmed entirely independently of any other module. Although this does introduce some inefficiency, it makes it possible to use program overlay extensively so that most of the available core memory may be dedicated to data areas. In addition to the command data, the control file contains all the input-output addresses for the experiment, as set up by an initiation program. This makes it possible to change the terminals for this experiment at will, or to use these programs for another experiment merely by changing a single table of I/O and disk file addresses.

A set of three programs has been prepared, one to execute previously prepared command strings, one to set up command strings from simple input data, and one to modify the command string sequence during the course of an experiment. The last two of these depend as much on our personal idiosyncracies and irrelevant details of the entire local laboratory organization as they do on the logical requirements of the paramagnetic resonance spectrometer; they are therefore not worthy of discussion other than as to delineation of their functions. However, since the organization of the execution program is almost independent of such irrelevancies, it includes many features of general applicability and deserves detailed description.

The execution program is schematized in Fig. 1, and consists of an entrance routine, an open-ended set of execution modules and an exit routine. Some of the modules are data-processing tasks after which the next instructions may be executed immediately. Others are timed control tasks handled by the monitor. After the latter are started by a call to the monitor subroutine INIO, and the control file is updated, control of the computer is relinquished to the monitor system, which assigns "foreground" service to the next user in a priority queue. When the timed control task is complete, the monitor re-enters the same program into the priority queue.

The first three modules explicitly use the control and timing facilities provided by the monitor system. In the first module the capability of the monitor system to close the loop in a simple servomechanism is exploited. Since at the start of a sweep the magnetic field may take up to a minute to stabilize (motion of a servomotor controlling the magnet power supply input voltage may be involved), the second module releases control of the computer for a while after setting the field to an initial value. In the third module are combined the development of the command sequence for recording a single spectrum and the logic of the computer-of-average-transients operation.

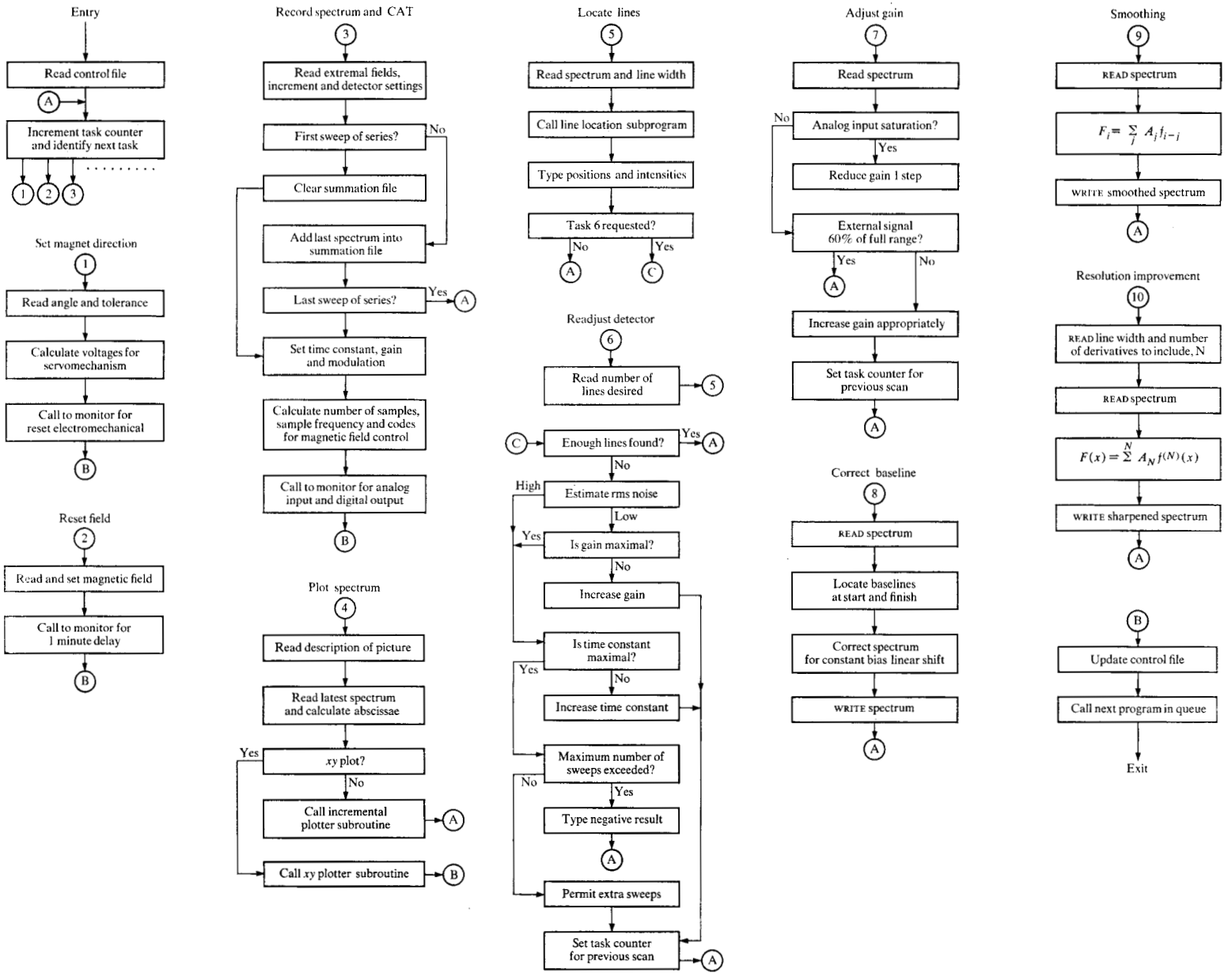
At the present time the desired output from the experiment is a table of the line positions and their intensities for each spectrum observed. Module 5 represents a preliminary attempt to provide the necessary algorithm. The line locator subprogram applies a series of tests to each segment of a spectrum to determine whether it represents the first derivative of an absorption line as conventionally displayed in EPR (Fig. 2), i.e., it should have extrema which significantly exceed the noise and the maximum should precede the minimum. The second integral of the line should exceed the noise level divided by the number of points used in calculating the integral. On a spectrum such as that in Fig. 2, where very few lines overlap, an algorithm based on these considerations works quite well; 17 of the expected 25 lines were found without any spurious entries appearing in the table. However, in spectra with much overlap, such as frequently occur when there are many hyperfine interactions, this algorithm becomes quite unreliable. We are considering more powerful methods, but have not yet discovered any adequate and simple one.

Modules 6 and 7 are the only ones in Fig. 1 which employ feedback to the experiment as a consequence of the data previously recorded. The first of these uses the line-locator module to check whether the number of lines seen exceeds that expected. If too few lines are found, the detector circuits are readjusted and another attempt is made to observe the desired spectrum. We have found that the effect of residual noise arising in the cable and the final dc amplification stages is minimized if the gain in early stages is increased. Module 7 adjusts the detector gain to the highest level possible without saturating the analog-to-digital converter at the computer.

Simple numerical transformations may often be employed to make the data-reduction tasks, whether they be performed by algorithms such as the line-locator or by hand, easier and more reliable. A common disturbing factor in paramagnetic resonance is baseline variation induced by electromagnetic pickup of the modulation signal by the cavity walls. We record each spectrum so that the ends of the sweep are in regions free of lines and use the mean baseline measured at each end of the spectrum to correct this error (Module 8). The remaining modules are examples of a large class of filtering operations, all of which can be expressed as polynomial transformations for discrete representations of stochastic processes. Two smoothing operations have been implemented, involving, respectively, local 5-point and 9-point fits of cubic polynomials.[14]

Another example of a useful transformation is line-

Figure 1 Flowchart, EPR Execution Program. All indicated reads and writes are to disk files.



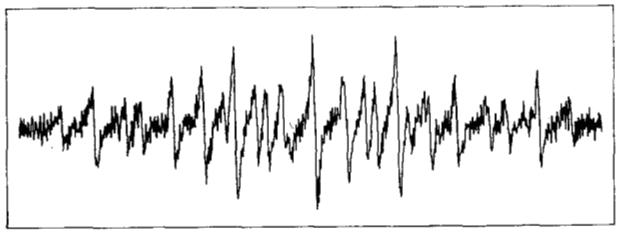


Figure 2 Example spectrum for line location tests.

Figure 3 Sample input command deck.

```
         16239 ZNF2/CU 1.2K 9465MC      40DB SUPERHET 12/13/67    TEST
   1    1-81.                  2500.     3000.       1.       001009
3 4-1
         16239 ZNF2/CU 1.2K 9465MC      40DB SUPERHET 12/13/67
   4   10 -81.  10.  0.   0.   2500.     3600.       1.       011009
3 410 9 4 5                               6.
```

sharpening. It has been shown previously[15] that if the line shape is known, there exists an integral transformation which provides a spectrum with improved resolution at the expense of signal-to-noise ratio. Usually this integral transformation may be written as a series of the even derivatives of the spectrum. The coefficients in the series are functions of the line shape and width. Because differentiation emphasizes noise, only the first few derivatives can profitably be included. We find this technique extremely valuable for spectra with many overlapping lines.

A flow chart for the initiation program has been given previously.[3] Besides taking input data convenient to the experimenter and expanding it to a command string appropriate to the execution program, it performs several elementary but important functions, such as checking the imput data for validity, correcting them where possible, and rejecting them where not. In addition, a number of tasks are entered into the input string automatically, since they are required precursors of tasks requested explicitly. To make possible restarts or starts after pauses, it also types task sequence numbers for key tasks. The interrupt restart program alters the task sequence counter, terminates the scan in progress and queues the execution program.

- *Sample Run*

Figure 3 illustrates a short input sequence; sets of three cards control observations and may be stacked up to 280 tasks, either explicity given or implied. Of course, several modules in Fig. 1 include loops back to earlier points in the command string, so that many more than 280 tasks may be executed. The first card of each sequence is simply identification of the experiment, which is entered on all plots and output typing. In the first set, the second card describes one scan at one magnet angle, −81°, from 2,500 to 3,000 gauss at 1 gauss intervals, with the detector set at 0.3 sec time constant (code 0), modulation 0.4 rms gauss (code 10) and relative gain 160 (code 9). Following the scan, the data are to be plotted (task 4) and the experiment is to wait for personal intervention (task −1). In the second set, four scans are to be averaged at each of 10 magnet angles starting at −81° with 10° intervals. Each scan is to be from 2,500 gauss to 3,600 gaus at intervals of 1 gauss. The detector settings are unchanged except for the time constant, which should now be 1 sec (code 1). At each angle after the scans are averaged, the data are to be plotted (task 4). Then the resolution is to be improved using a linewidth estimate of 6 gauss for the transformation (task 10), and the resulting data are to be smoothed with the 9-point algorithm (task 9). After the revised data are plotted, a search for lines is requested (task 5).

A very small portion of the output from a recent study is illustrated in Figs. 4 and 5. The sample under observation is ZnF_2 substitutionally doped with Cu^{++}. The first half of Fig. 4 is the typed image of the input requests, obtained on an output typewriter in the laboratory. The lower part of the figure is the description of operations at the time of execution. The spectrum illustrated is one collected at 1.2°K. The top trace is the original spectrum averaged over 4 scans. The lower portion is a replot after numerical resolution improvement and smoothing. These records are pasted directly into the laboratory notebook and, with very little supplementation, give a more complete and more accurate record than has previously been usual.

Figure 4 Sample experimental record.

```
START AN EPR SEARCH

                ZNF2/CU 4K 20DB 40UAMP  X DIR.  16239-59 12/4/67  TEST RUN
   1 SWEEPS        1 ANGLES -81.0    0.0    0.0    0.0    0.0
FIELD 2500.0 GAUSS TO 3000.0 GAUSS IN STEPS  1.00 GAUSS
TIME CONSTANT  0   MODULATION 10   GAIN  9
TASKS  -81.  2   4   1
JOB   5 IS A PAUSE

          ZNF2/CU 4K 20DB 40UAMP  ROTATE  16239-59 12/4/67
   4 SWEEPS       10 ANGLES -81.0   10.0    0.0    0.0    0.0
FIELD 3000.0 GAUSS TO 3600.0 GAUSS IN STEPS  1.00 GAUSS
TIME CONSTANT  1   MODULATION 10   GAIN  8
TASKS  -1.  2   5   9  11   3   8
     -81. BEGINS AT JOB   5
     -71. BEGINS AT JOB  12
     -61. BEGINS AT JOB  20
     -51. BEGINS AT JOB  28
     -41. BEGINS AT JOB  36
     -31. BEGINS AT JOB  44
     -21. BEGINS AT JOB  52
     -11. BEGINS AT JOB  60
      -1. BEGINS AT JOB  68
       9. BEGINS AT JOB  76


POSITION MAGNET TO  -81.0    0.0 DEGREES AT  2.716 HRS.
SET FIELD TO  2500.0 GAUSS
READ AND AVERAGE   SPECTRUM    1 OF    1 AT  2.774 HRS
FIELD FROM 2500.0 TO 3000.0 IN STEPS   1.0 GAUSS
TC  0.3 SECONDS     MOD   0.360 GAUSS    GAIN   160.
REVISED INCREMENT   0.91          546 POINTS
PLOT ON CALCOMP PLOTTER
-81.  0.  ZNF2/CU 4K 20DB 40UAMP  X DIR.  16239-59 12/4/67  TEST RUN

RESTART EPR SEARCHES AT JOB      5
SET FIELD TO  3000.0 GAUSS
READ AND AVERAGE   SPECTRUM    1 OF    4 AT  2.930 HRS
FIELD FROM 3000.0 TO 3600.0 IN STEPS   1.0 GAUSS
TC  1.0 SECONDS     MOD   0.360 GAUSS    GAIN   100.
REVISED INCREMENT   0.91          656 POINTS
SET FIELD TO  3000.0 GAUSS
READ AND AVERAGE   SPECTRUM    2 OF    4 AT  3.144 HRS
SET FIELD TO  3000.0 GAUSS
READ AND AVERAGE   SPECTRUM    3 OF    4 AT  3.361 HRS
SET FIELD TO  3000.0 GAUSS
READ AND AVERAGE   SPECTRUM    4 OF    4 AT  3.588 HRS
PLOT ON CALCOMP PLOTTER
-81.  0.  ZNF2/CU 4K 20DB 40UAMP  ROTATE  16239-59 12/4/67
SHARPEN W=  6.0      2 DERIVATIVES
 9-POINT SMOOTHING
PLOT ON CALCOMP PLOTTER
FIND LINES IN DERIVATIVE SPECTRUM    LINE WIDTH   5.000
3033.8 0.1E 05 3308.1 0.9E 04 3326.8 0.1E 05

POSITION MAGNET TO  -71.0    0.0 DEGREES AT  3.873 HRS.
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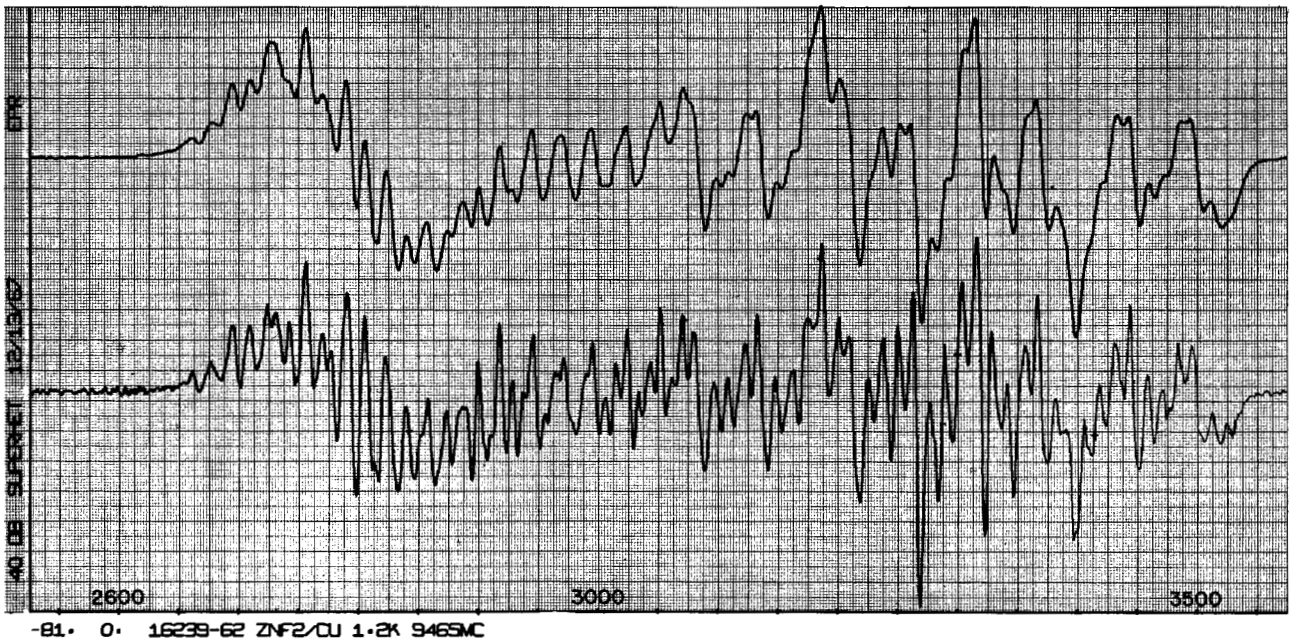

Figure 5 Sample spectrum: Cu^{++}-doped ZnF_2, along a ⟨110⟩ crystal axis.

Discussion

With electron paramagnetic resonance as an example, some of the principal, generally applicable elements of computer-assisted spectroscopy have been discussed. We have tried to show that, both for the interfacing hardware and for the majority of associated programs, the similarities among slow-scanning laboratory instruments make it possible to transfer methods, programs and sometimes even electrical interfaces[16] from experiment to experiment with at most trivial changes. Throughout, there has been the supposition that what was desired was a system in which certain feedbacks dependent upon the observations could control the future course of the experiment automatically. At the rudimentary level presently implemented, this has not proved significantly more difficult to design than a simple data-logging system.

Simple examination of the instruments in question shows that the necessary controls are those for an independent, swept variable; for one or two stepped parameters, and for several signal detection circuit variables. With a local/remote relay wherever a computer-controlled switching circuit parallels a spectrometer panel control, the stand-alone capability of any instrument can be preserved. The independent variable circuits do vary from experiment to experiment, but the signal circuitry seems to be quite standard. Moreover, the logical requirements of all these circuits are so similar that it has been possible to provide, as a monitor program function, a single subroutine capable of commanding repetitive data-collection and control for multiple experiments time-shared in real time.[3]

One or two comments about the economics of a hard-wired interface to a remote (250 ft) computer are perhaps of interest to the reader. Inclusive of cables (76 conductors, twisted pairs individually shielded) and of the modifications necessary to the magnetic field control circuitry, less than $1,000 worth of commercially available electronics parts was required.[16] In addition, we have an output typewriter in the laboratory; this is presently shared (by dividing the page vertically) with one other experiment and will be used for a third experiment in the near future. On the time-shared IBM 1800, the duty cycle during observation of a spectrum is of the order of 0.1%, and three or four minutes of foreground processing time are required to ameliorate and plot the output. Most of this time is associated with mechanical motion of the incremental plotter and could be avoided by properly buffered plotter control. The incremental plotter is, of course, shared with all the experiments connected and also with normal job-stream activity on the same computer. Our computer is being run without a machine operator, i.e. open shop. In spite of the rather large number of individuals involved, the operation has been relatively trouble-free after the users were taught to avoid such drastic procedures as erasing core memory to execute restarts.

That the user's programs described have an applicability to multifarious experiments depends on the fact that all scanning instruments have as their primary data stochastic processes, i.e. variables in time with a random noise component. It is possible to identify a small number of

operations which comprise an adequate set for this class of experiments, e.g., reset of independent variable(s) and wait for stability, scan an independent variable and collect a dependent variable, perform one of a set of integral transformations on a stochastic set, and perform a "best fit" of a physical model to some of the features of a stochastic set. Most of these operations can and should be programmed entirely independently of the source of the scan. Then, if the control program is organized to allow execution of such operations in any order, it can itself be directed by relatively simple programs tailored to the particular experiment and experimenter. It is even possible to program and debug extensions to the operation repertory while the experiment is running. Although other program organizations may be simpler, we recommend similar methods for experiments for which there is a premium on flexibility.

The availability of the computer link and the associated programming has qualitatively improved our paramagnetic resonance studies. Previously, we spent the majority of our time performing the experiments and the minority considering the results and planning the next experiments; presently the emphasis is reversed. More specifically, for the analysis of spectra as complicated as that illustrated in Fig. 5, detailed comparison with spectra computed from estimated spin Hamiltonians is necessary. That the experimental record now has essentially negligible plotting errors and is available repeatedly at precisely the same scale has converted what was previously an uncertain and time consuming procedure to a trivial one. We are making extensive use of averaging and smoothing to improve key regions of spectra and to search for otherwise hidden signals in new samples. The numerical improvement of resolution has, on more than one occasion, provided hints that led us to the assignment of an otherwise hopelessly complex spectrum (there being 240 lines in the spectrum of Fig. 5). Of course, individually many of the required functions can be implemented with special purpose hardware, but when all of them, with anticipated but unspecified extensions, are the objective, the authors believe that online computation is the simplest, most flexible and most trouble-free possiblility.

Many of the techniques for processing spectral data by on-line computation have not been discussed in this paper. In many cases they are already adequately described in the literature.[17] We have also avoided discussion of man-machine interactions in connection with laboratory automation, since our methods in this area are still ad hoc and quite crude. This is a subject that should receive much attention in the near future. The elements of novelty which we have attempted to convey relate to the close similarities, from the vantage point of a digital computer, between superficially diverse experiments, and to elements of logical and physical organization that make it possible, without significantly sacrificing flexibility, to run an instrument either mostly automatically or with as much personal control as may be deemed desirable.

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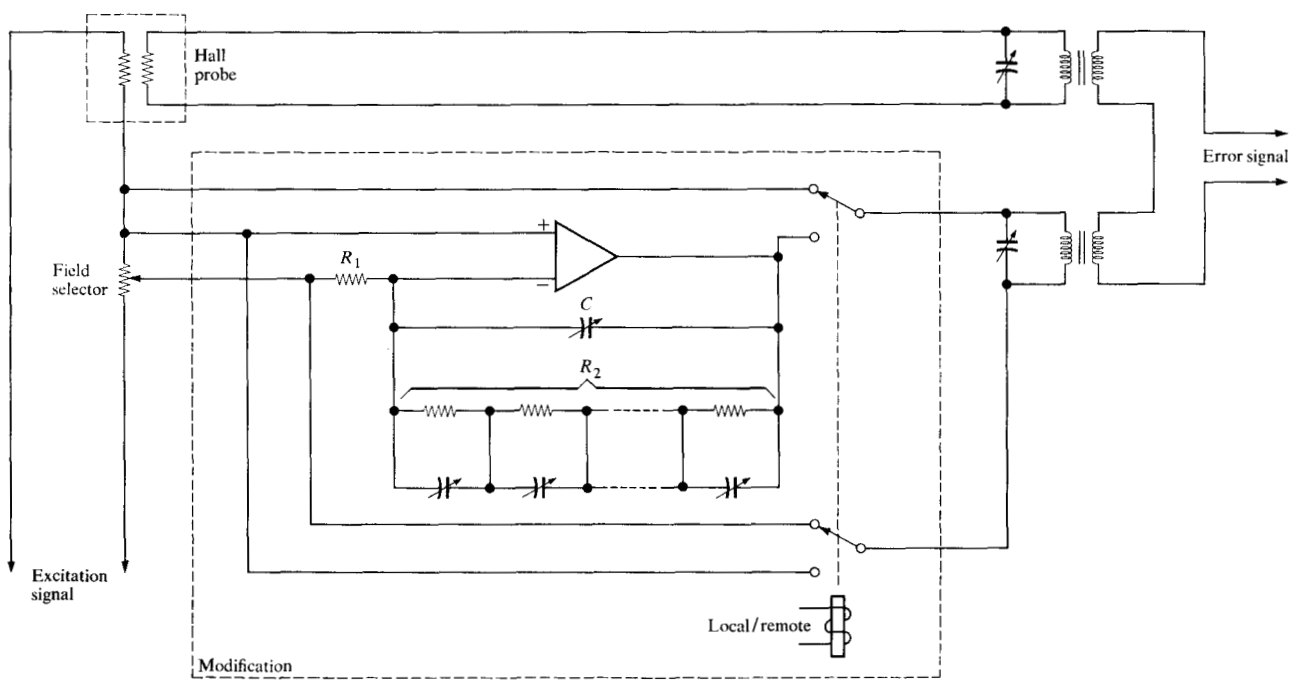
References and footnotes

1. For an instrument used in more routine analytical problems the physical and logical controls may be considered a subset of those necessary for a research instrument. We leave it to the reader to identify the economies possible for his particular situation, but suggest that the flexibility required for a research instrument is mirrored by the slightly differing requirements of the members of a set of analytical instruments.
2. Recently several proposed systems for data-logging without any feedback control have been described to us. We have not found it markedly more difficult to include control functions and felt that the most exciting possibilities are forfeited by the more limited approach. For scanning instruments it is necessary to interface the independent variable to the computer, either with a readout device or with a control device driven from the computer. Contrary to several opinions we have heard, we feel that, for the precision we desire, the latter alternative often has simpler circuitry and at the same time allows significant simplifications to the associated programming.
3. H. M. Gladney, *J. Computational Physics* **2,** 255 (1968).
4. Of the instruments being considered for automation, slow-scanning apparati constitute the majority, both with respect to numbers of instruments installed and with respect to numbers of types of instruments. In one large biomedical laboratory we have visited, 100 out of 105 instruments being considered for automation belonged to this class, which includes grating and prism spectrometers in all energy ranges, magnetic resonance spectrometers, some mass spectrometers, scanning microdensitometers, chromatographs, and a wide variety of apparati for rate studies of physical and chemical processes.
5. In this paper, "spectrometer" will refer to any instrument with the characteristics described in this section.
6. This feature is primarily important because it eliminates possible timing interferences of different experiments controlled by a single computer. It, of course, implies that the processing arithmetic be based on finite difference formulas for stochastic data on unequal intervals. A possible solution, which we are employing for our vapor phase chromatograph, is to interpolate to equal intervals as the first computational step.
7. In some experiments there are advantages to processing during collection, but often these can be otherwise implemented, either with repetitive scans or with strategies peculiar to the situation. For example, we have avoided the necessity of automatic gain control in vapor phase chromatography by using two analog inputs and a voltage divider and selecting the appropriate intensity during computation.
8. A simple RC-filter following an amplifier may be considered a phase-sensitive detector at zero frequency.
9. K. Foster, D. M. Hannon and D. Horne, *IBM J. Res. Develop.*, this issue.
10. J. P. Goldsborough and T. R. Koehler, *Phys. Rev.* **133,** A135 (1964), describe the instrument.
11. M. P. Klein and G. W. Barton, *Rev. Sci. Inst.* **34,** 754 (1963); R. R. Ernst, *Rev. Sci. Inst.* **36,** 1689 (1965).

12. An "interrupt" is a signal, which, when received by the computer, starts an associated program at once, subject only to the requirement that no higher priority interrupt program is in execution.
13. P. M. Grant of this laboratory has confirmed our indirect observations by noise level measurements. With RC filtering of 0.3 sec rms, noise levels of $\sim$ 0.01 volt were measured. This observation is, of course, only relevant to "slow" instruments. The only problem that arose was noise from a ground loop in the main signal line. It disappeared when a spurious second ground was disconnected.
14. For spectra recorded with about 15 points/line we find that the 5-point smoothing is not very helpful, but that the 9-point formula
$$Y_i = \{59\ y_i + 54\ (y_{i-1} + y_{i+1}) + 39\ (y_{i-2} + y_{i+2}) + 14\ (y_{i-3} + y_{i+3}) - 21\ (y_{i-4} + y_{i+4})\}/231$$
provides significant improvement without decreasing the apparent resolution.
15. L. C. Allen, H. M. Gladney and S. H. Garum, *J. Chem. Phys.* **40,** 3135 (1963).
16. All the connections to the computer are routed through a distribution panel at the EPR spectrometer. At one point we probably used this panel to help debug the optical spectrometer. Wiring diagrams are available from the authors.
17. Illustrations of the efficacy of "catting" are provided by the manufacturers of special purpose signal-averaging equipment, and by W. D. Gwinn, A. C. Luntz, C. H. Sederholm, and R. Millikan (to be published). Least-squares fit to stochastic signals has been discussed by W. D. Keller, T. R. Lusebrink and C. H. Sederholm, *J. Chem. Phys.* **44,** 782 (1966), for NMR spectra and by J. Pithra and R. N. Jones, *Can. J. Chem.* **44,** 3031 (1966) for IR spectra. In the latter paper extensive tests of convergence rates of various iterative algorithms are explored. Corrections for finite slit widths, R. N. Jones and R. Venkatarghavan, *Spectrochimica Acta* **23A,** 941, 925 (1967), are closely related to numerical resolution improvement (Ref. 15). More recently, Jones discusses automated IR spectroscopy, *Jap. J. Chem.* (to be published).

Figure 6 Digital control circuit for magnetic field. The part of the circuit inside the dashed line has been added to the Varian Fieldial. The resistance R_2 is a precision binary summation array switched by reed relays driven by the computer. The capacitor C eliminates spurious oscillations. Note particularly that with the "local/remote" relay unenergized the circuit is identical to that before these modifications. This method was used wherever additional switching circuitry was added to the spectrometer (e.g., in the detector controls). All local/remote relays are enslaved to a single panel switch; when this switch is in the local position, the spectrometer runs entirely independently of the computer.



Appendix I: Magnetic field control

Computer control of the magnetic field was obtained with a modification of the Varian Fieldial control by the ac Hall effect; a schematic of the result is shown in Fig. 6. The probe excitation current is passed through a precision voltage divider whose output is opposed to the Hall voltage to obtain an error signal. Between the voltage divider and the transformer bridge we have interposed a conventional operational amplifier circuit whose gain is accurately proportional to the feedback resistance. The feedback resistor is a precision binary summing array bridged by shorting reed relays which are controlled from one of the digital output groups of the computer. After trimming, this circuit gives as accurate control as the Fieldial itself can provide. To provide completely automatic field control an additional minor change of the magnet power supply was necessary. This kind of supply usually has an autotransformer controlling the input voltage to the rectifier tubes. The input voltage must be adjusted manually to a value suitable to the desired magnet current. In our application this was accomplished by an electromechanical servo entirely internal to the power supply. A simpler method for control in newly designed power supplies would use saturable reactor rather than autotransformer input.

Positioning of the electromagnet is achieved by a conventional electromechanical servomechanism for which the computer provides the necessary feedback logic. An appropriately-geared 0.2% linear potentiometer, with vernier adjustment for zeroing, is mounted on the rotation axis of the magnet. At the periphery an ac motor drives the magnet at 10 degrees per minute with rack-and-pinion gearing. With dc braking the rotation stops within 0.1 degree. The maximum positioning error, 0.2 degrees, is acceptable.

Appendix II: A digital-output multiplexor

While several spectrometers were in preparation for automation, a requirement developed for more digital output words than our computer provided at that time. No simple circuit available in the literature* answered our requirement. As exemplified above, each spectrometer seems to require about one digital output word (16 bits) for control of subsidiary parameters, detector settings and analog plotters. This word requires resetting not more often than every few seconds, and more commonly only every few minutes. When several of these digital outputs are close together, but remote from a central computer, the cost and inconvenience of a dedicated digital output word and a long multiple conductor cable for each laboratory output word can be avoided. In addition to the AND gating required for input multiplexing, output multiplexing requires a memory for each laboratory output†. This appendix describes a very simple, economical and reliable circuit to accomplish this function.

* Many circuits for data acquisition multiplexing and time-multiplexing with latching relays have been described but are not applicable.

† The function we describe can be accomplished with latching relays, but only at about twice the expense of the present circuit and with provision for unlatching signals as well as information signals.

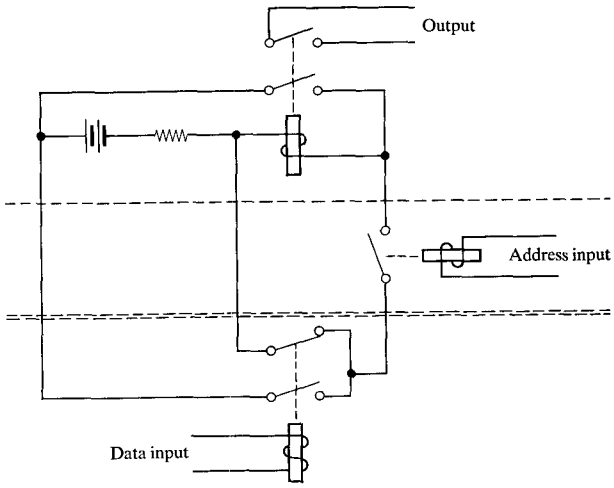


Figure 7 Basic circuit for digital-output multiplexor. The circuit has both switching and memory functions.

The elementary circuit, which is multiply replicated in a complete digital-output multiplexor, is illustrated in Fig. 7. It has the property that if the address input is energized, the output assumes the same value as the data input, but if the address input is de-energized, the output remains at the last value set. Both sides of the output are isolated. For N output words of n bits each, the part of the circuit above the dotted line is replicated (nN) times; the portion below the double dotted line is replicated only n times. The address input becomes an AND-gating addressing array. To avoid interference among output groups it is necessary to provide one dummy address, so that all output groups may be disconnected while the data input is switched. The number of digital bits required as input is $[n + \log_2(N + 1)]$.

A prototype‡ of this multiplexor, with 15 output groups of 16 bits each, has been built and is operative in this laboratory as part of the interface for several spectroscopic experiments. It uses commercially available reed relays as the switching elements; these are reliable at frequencies of up to 300 Hz so that switching speeds are no problem for the applications in question. In fact, the limiting rate of switching is imposed by the computer subprograms which we find convenient for control of the multiplexor. Tests up to 30 words/sec were satisfactory.

‡ A detailed circuit diagram and a IBM 1800 program to provide convenient control for this device are available from the authors.

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