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Computer Control in Chemistry at the Lawrence Radiation Laboratory[1]

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ABSTRACT

The Chemistry Department at the Lawrence Radiation Laboratory has been engaged in the use of digital control computers as an integral part of laboratory experiments. These computers not only provide control and data acquisition functions, but also result in improved accuracy and the ability to perform more advanced experiments.

This paper describes two of the eight systems currently in use in the Chemistry Department. One is a PDP 8/S dedicated to one experiment at a time while the other is a time-shared PDP-7. The differences in operation and application of each will be surveyed and the advantages and disadvantages compared.

INTRODUCTION

Approximately three years ago the Chemistry Department at the Lawrence Radiation Laboratory (LRL) started investigating the use of digital control computers to improve the chemistry capabilities. These computers were to be used for the control of chemistry equipment and perform data acquisition functions including on-line computations [1]. The first such computer purchased was a PDP-7[2] to be time-shared in the Analytical Section. Since that time, we have added to our capabilities several smaller computers to be used as described below.

The use of computers in chemistry enables the chemist to save time, improve accuracy and add new experimental dimensions. In addition, the computer allows the chemist to close-the-loop in experimentation. That is, the direction of the experiment can be changed at any time during the experiment, the change being based upon all the information collected up to that time. In addition to implementing the above, we at LRL are comparing the use of time-shared systems vs. the use of small dedicated computers. To date it has been our experience that the larger time-shared computer has certain disadvantages. Chief among these are the

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[1] This work was performed under the auspices of the U.S. Atomic Energy Commission.

[2] Manufactured by Digital Equipment Corp., Maynard, Massachusetts.

political implications and programming. For every time-shared computer there must be one strong-minded scientist to guide and direct the overall project. It is obvious that two strong-minded and strong-willed scientists will have great difficulty in working with a time-shared computer simultaneously. Although the smaller dedicated computer concept may have obvious hardware limitations, it allows complete freedom for the scientist.

This paper will discuss in detail only two specific implementations and their relative merits. The first is the PDP-7 used as a time-shared controller. The second is the small PDP 8/*S* which is being used as a dedicated computer interfaced to only one experiment at a time.

COMPUTER USAGE IN THE CHEMISTRY DEPARTMENT AT LRL

Below is a listing of the digital control and data acquisition computers now in use at the Lawrence Radiation Laboratory. These are listed in the chronological order of purchase.

PDP-7: A time-shared system in the Analytical Section of the Chemistry Department. This computer has to date been interfaced to a 3-column chromatograph [2], a vacuum apparatus for the simultaneous determination of carbon, hydrogen, and nitrogen in organic compounds [3]–[7], and a vacuum fusion apparatus for the determination of trace quantities of oxygen, hydrogen, and nitrogen in metals. This latter apparatus includes a small mass spectrometer for gas analyses. In addition to the above, interfacing has begun for a CEC 21-103C mass spectrometer, a spectroscopic-plate reader, a fluorimeter and for certain electrochemical experiments.

PDP-8: Interfaced to a Picker Nuclear x-Ray Diffraction Unit. This computer controls the single crystal orientation and is also used for data acquisition.

PDP-8: For control and data formatting in nuclear spectroscopy.

PDP-8: For microdensitometer control and data acquisition. This computer is used to read the plates obtained from a spark source mass spectrometer.

PDP-8/*S*: For research. This control computer is used as part of our feasibility experiments, as a small dedicated computer interfaced to a single experiment. It will be discussed in some detail in a later part of this paper.

PDP-8: For an electron microprobe data acquisition.

PDP-8: For mass spectrometer control and data acquisition. This computer will be time shared for control and data logging from two surface ionization mass spectrometers. In addition, the computer will be used for ensemble averaging and on-line dynamic dead time corrections.

(PDP-9): For control in chemical-engineering research. It is to be used in rock stress strain tests, creep tests and particle size analyses.

From the above it is readily apparent that we are in general attempting to use small machines dedicated to a single task, rather than larger timeshared systems.

TIME-SHARED CONTROL COMPUTER

In Analytical Chemistry we are using a digital computer for time-shared control and data acquisition. The computer chosen was the PDP-7 having a word size of 18 bits and a memory reference time of 1.75 μsec. It has 8K of core memory, an IBM compatible tape deck and an extended arithmetic element for fast computations. In addition, the computer has a variable boundary register, oscilloscope display, 1-kHz clock and a single level interrupt. Figure 1 is a schematic diagram of our present system. The dotted lines represent interfacing that is in progress but not yet complete.

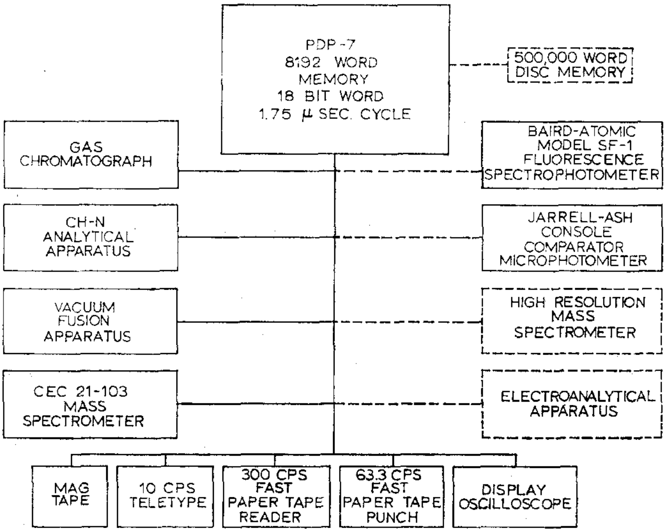

FIG. 1. **Schematic Outline of the PDP-7 time-shared system.**

The gas chromatographic apparatus that has been interfaced to the computer was designed and built at LRL. This chromatograph has three columns, three detectors and a controlled inlet system for the introduction of three different samples or standards. The columns can be temperature programmed from −180°C to +250°C. They can also be run in many parallel and series configurations. Control of the columns and the inlet system is accomplished by means of six, 7- or 6-way valves. Sample pressures are measured by a digitized pressure transducer having a resolution of 18 bits. All functions of this chromatograph can be controlled manually or fully automatically via the digital control computer.

Three methods of data acquisition from the chromatograph have been tested under computer control [8].

In the first, the signal of the thermistor detector bridge combination was measured by a servo-driven potentiometer and shaft-angle encoder combination. The output of the shaft angle encoder is converted from gray to binary code by a hardware system. The unit has a resolution of 1 part in 21,000. Figure 2 shows a typical output obtained from this unit for a nitrogen peak as eluted from a 5A molecular sieve column. The other two methods tested were a voltage-to-frequency converter and counter combination, and an analog-to-digital converter preceded by an amplifier. A summary of this data is given in Table I. Note that the lack of any inherent integrating characteristics in the particular hardware used for data acquisition can result in increased standard deviation.

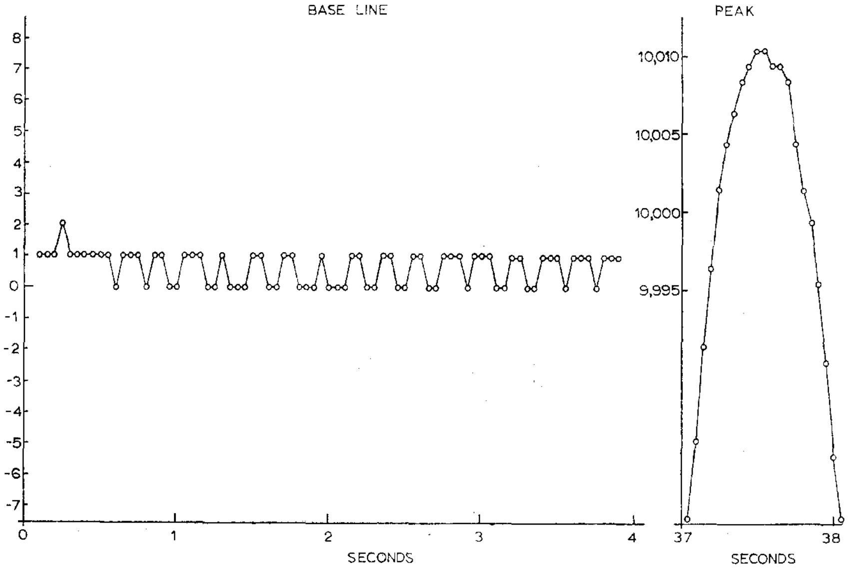

FIG. 2. Gas chromatography peak and base line obtained under computer control via a servo-driven potentiometer.

TABLE I

Comparative Data For Three Methods of Data Acquisition

Standard Deviation; Linear time fit of results; no smoothing or filtering

Digitizing Method	Peak Height	Integral
Millivolt-potentiometer shaft encoder	0.02%	0.08%
Voltage-to-frequency converter	0.04%	0.55%
Analog-to-digital encoder	0.12%[a]	—

[a] No apparent trend.

An apparatus for the simultaneous determination of carbon, hydrogen and nitrogen in organic compounds by a gas manometric method has been fully automated. This is a high vacuum glass apparatus as shown schematically in Figure 3. All valve manipulations, toepler pump control, cold trap temperature control, and data acquisition from the pressure transducer are performed under computer control. As a general description of the analytical procedure, 3-5 mg. of

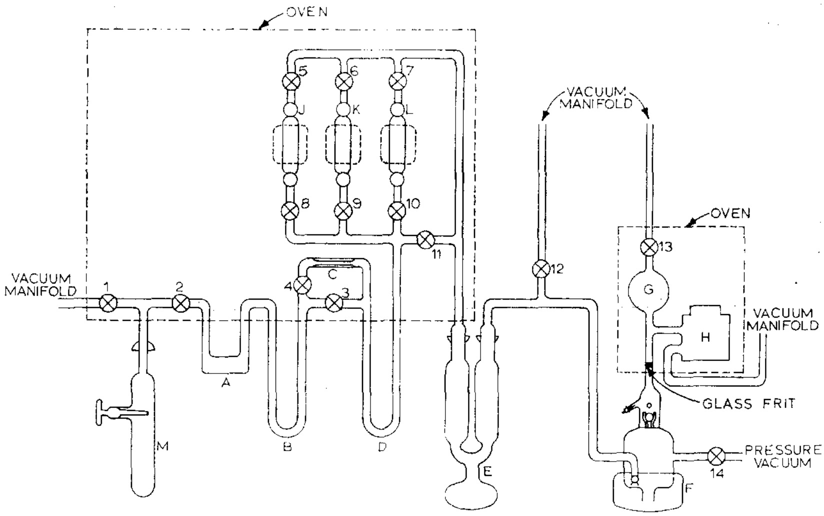

Fig. 3. Apparatus for the simultaneous determination of carbon, hydrogen and nitrogen in organic compounds. A. Cu–Hg Amalgam; B. −100°C Cold Trap; C. Glass Restrictor; D. −196°C Cold Trap; E. Hg Transfer Diffusion Pump; F. Rodder Type Toepler Pump; G. Glass Burrette; H. Pressure Transducer; J. 250°C Uranium Trap; K. 800°C Uranium Trap; L. 150°C Manganese Dioxide Trap. Valves 1–13 are automated, hermetically sealed glass valves.

the sample (gas, liquid or solid) to be analyzed is weighed into a quartz tube along with one gm. of copper oxide. The tube is then evacuated, sealed and fired at 925°C. Upon cooling the bomb is transferred to the vacuum analytical apparatus, opened and the combustion products, namely the CO_2, H_2O and nitrogen are separated and measured.

Temperature control in the traps B and D is performed by the computer. Teletype control of one word in the program allows the chemist to change trap B to any new temperature desired between −180°C and +100°C. In addition, the inlet of each trap contains a short zone where multiple sublimation-condensation stages can be performed under computer control.

The pressure in the gas buret G is measured by means of a 0 to 10 torr full scale MKS Baratron[3] pressure transducer. The pressure is digitized and is reproducible to one part in 32,000. Table II lists typical results of CHN analysis obtained via computer control. The upper results shown in Table 2 were obtained using manual

TABLE II

TYPICAL RESULTS OF CHN ANALYSIS VIA COMPUTER CONTROL

Compound	Carbon % Found	Carbon % Theoretical	Nitrogen % Found	Nitrogen % Theoretical	Hydrogen % Found	Hydrogen % Theoretical
			Manual Readout			
P-di-N-Nitrobenzene	42.88		16.65		2.30	
	42.88		16.65		2.45	
	42.82		16.60		2.35	
Average	42.86	42.87	16.63	16.67	2.37	2.40
			Fully Automatic			
P-di-N-Nitrobenzene	42.90		16.64		2.38	
	42.89		16.62		2.46	
	42.89		16.66		2.50	
Average	42.89	42.87	16.65	16.67	2.45	2.40
Acetanilide	71.02		10.30		6.56	
	71.06		10.41		6.75	
	71.04		10.38		6.79	
Average	71.04	71.09	10.36	10.36	6.70	6.71

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[3] MKS Instruments, Inc., 45 Middlesex Turnpike, Burlington, Mass.

readout of the pressure transducer together with computer control of the rest of the instrument. The lower results were obtained under full automation. With additional experience, we believe that routine determinations can be made with a standard deviation of less than 0.03 wt. %.

A vacuum fusion apparatus for the determination of traces of oxygen, hydrogen and nitrogen in metals has also been fully automated. All valve manipulations, sample introduction, pressure measurements and gas analysis are performed under computer control. The gases evolved are analyzed by a small mass spectrometer.[4] This spectrometer can be fully controlled by the computer. The data acquisition from the mass spectrometer is by means of a 1-MHz voltage-to-frequency converter and binary counter. Figure 4 is a schematic of the system.

The above apparatuses have been interfaced and the first two systems are currently in operation, and the third in an advanced state of debugging. Interfacing

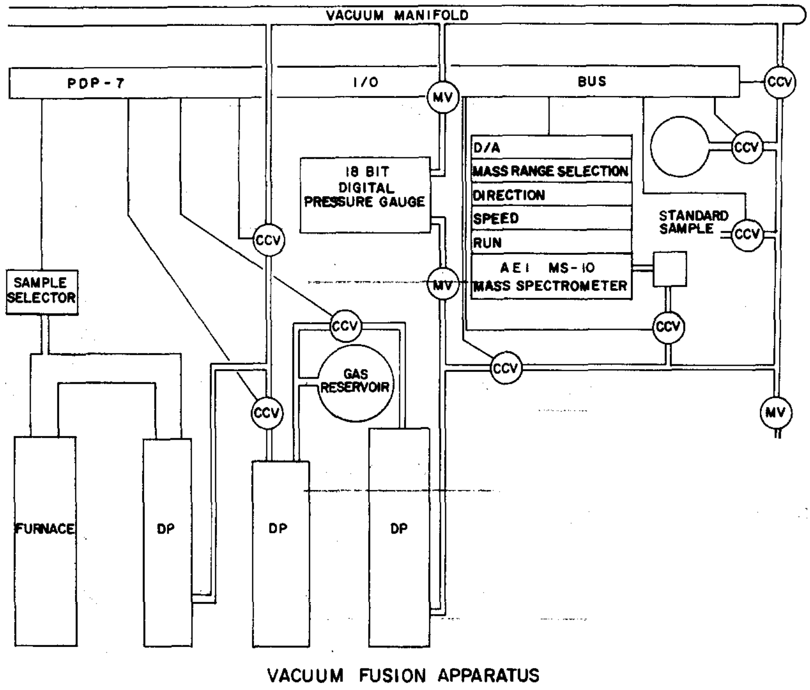

FIG. 4. Vacuum fusion apparatus. CCV—Computer-controlled valves; MV—Manually controlled valves.

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[4] MS-10 Mass spectrometer. Manufactured by Associated Electrical Industries Limited, Barton Dock Road, Urmston, Manchester, England.

has begun for the CEC 21-103C mass spectrometer, the spectrographic-plate reader, the fluorimeter and electrochemical apparatuses. Additional experiments will be added until the maximum capacity of the system is reached. We currently anticipate that the capacity of this system will be a minimum of ten such experiments or instruments. In addition, data acquisition from a fast-scan, high-resolution mass spectrometer will be performed in other than a time-shared mode (all other experiments will be delayed for the duration of the sweep). The data from the high-resolution mass spectrometer will be transferred to disc storage for subsequent processing.

DEDICATED CONTROL COMPUTERS

An alternative method to instrumental control is the use of a dedicated computer. In this case the actual processor need not be as large or as fast as that required by the time-shared system described earlier in this paper. In fact, almost any of the general-purpose word-oriented binary machines currently being manufactured are more than capable of control and data acquisition for most chemical instruments. The largest exception to this statement lies in the area of high-resolution mass spectrometry. Here the data rate and bulk information size often preclude the use of the small general-purpose computer.

Spectroscopic ensemble averaging will be used to illustrate the use of a dedicated computer in a chemistry laboratory. The spectrometer used was a Cary Model 14 and the computer a PDP-8/S. The two instruments were interfaced using a breadboard digital and analog network.

This interface is actually hybrid (combined digital and analog). A block diagram of the interface is shown in Fig. 5. The signal is not merely digitized and then processed, but is refined in analog fashion under digital control prior to analog-to-digital conversion. The interface minimizes the bandwidth of the system to the capability of the system prior to digitization. In addition it also synchronizes the computer to the experiment. The signal is taken directly from the photomultiplier preamplifier in the spectrometer, bypassing the rest of the spectrometer electronics.

The reference signal is integrated for a fixed length of time and then digitized. Then the background signal is integrated for the same length of time and digitized. Finally the data signal is also integrated for the same length of time and digitized. Mathematical corrections are then performed by the computer.

In addition, the interface detects unit Angstrom changes in the wavelength and interrupts the computer for appropriate data modification. If needed, this digital value can be read by the computer to determine the exact wavelength. This, however, is not done at every change due to the length of calculation time required. Only changes are recorded, and absolute values checked at the beginning of each sweep.

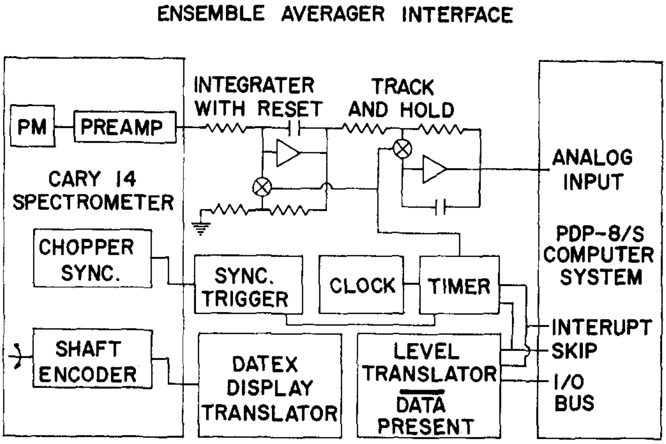

FIG. 5. Interface for the ensemble averager.

In this manner the spectrum can be multiply scanned and the corresponding signals averaged for an increase in detectability or signal-to-noise ratio.

Figure 6 shows an oscillograph of the electronic waveforms obtained from the system. The first is the synchronization signal, the second is the preamplifier output signal, the third is the gating or timing signal, and the fourth is the integrator-track and hold output. It is this latter signal that is digitized.

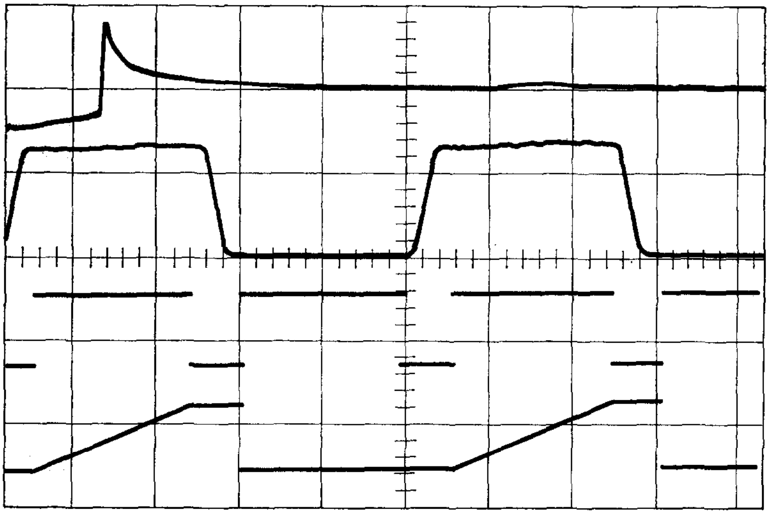

FIG. 6. Oscillograph of interface waveforms.

This interface synchronizes the computer to the spectrometer via the interrupt facility. The interrupt causes the computer to perform a certain alternative program whenever an external signal occurs. During the remainder of the time, the computer displays the accumulated data.

The program processes the data by subtracting the background from data and reference values, then dividing the data value by the reference value to normalize the results and finally summing the results in wavelength phase coherence. Initial data is 12-bit binary, but the sum is a 24-bit 2's complement number. This utilizes double precision arithmetic. However, this small machine is capable of such processing at least 60 such sets of data per second. In addition it keeps a record of the wavelength and displays the data in the unused time. At the end of a run, the program can punch out the data on paper tape. All operations are performed under the control of a teletype initiated controller. This method is extremely versatile in mathematical processing techniques and can be changed from experiment to experiment by merely reading in a new program or changing operating parameters from the teletype.

These applications show a few of the capabilities of control computers in the chemistry laboratory. While they are not the most imaginative examples of computer utilization, they are useful applications and constitute a reasonable starting point from which more sophisticated computer utilization can be undertaken. In addition, we have shown that alternative methods are available to solve instrumentation problems, i.e., there is no unique solution. While there may be many wrong solutions, there is no "right" solution. The best solution is dependent upon the specific problem and personnel involved in solving that problem.

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