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High-Performance Digital Timing System

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The design of a high-performance timing unit is described. The underlying principle of operation is that the time of a signal in a given 5-ns period is determined by its position on a delay line having eight taps. This results in a precision of $^5/_8$ ns. The eight taps constitute the bits of an eight-bit word, the value of which is recorded in flip-flops. Four such eight-bit words are combined to give a 32-bit word representing the time of the signal in a 20-ns period. The number of 20-ns periods is counted by a 16-bit counter giving a dynamic range of 0–1.3 ms. The times of 15 events occurring in one timing period (up to 1.3 ms) can be determined and stored. The apparatus has been constructed and placed in operation; performance tests showing that it meets specifications are given. Illustrative mass spectra obtained by using the unit in a ^{252}Cf time-of-flight mass spectrometer are also given.

In a novel form of mass spectrometer developed by Macfarlane and Torgerson (*1*) ionization and volatilization of a sample are accomplished by high-energy fission fragments emitted from spontaneously fissioning californium-252. One fission fragment passes through a thin metal foil, one side of which is coated with the compound of interest. The passage of the fission fragment effects the volatilization and ionization of the sample. The ions produced are accelerated and mass identified by a time-of-flight technique. The complementary fragment is used to indicate the occurrence of a fission event and to provide a reference for measuring the ion flight time.

The technique is of much current interest to research in biochemistry and medicine since it allows the mass determination of large, highly involatile molecules. We in this laboratory are much interested in these measurements, and we have therefore constructed such a mass spectrometer. The instrument used by Macfarlane and Torgerson utilized the time-of-flight method of mass determination, and we have followed their lead in this regard. The time-of-flight method is particularly suited to the ^{252}Cf method of ionization because (1) the ionization intensity is quite low, which dictates a time integrating, pulse counting method of mass determination and ion detection, and (2) the start time may be determined from the complementary fission fragment with a high degree of accuracy (on the order of a nanosecond). In principle this allows ion flight times to be determined with a high degree of accuracy, from which accurate ion masses and atomic compositions may be obtained.

The substances of particular interest for investigation using this apparatus can have high molecular weights, and thus we wished the mass range of the apparatus to extend to several thousand daltons. We furthermore wished to have the capability of measuring complete spectra with adequately high resolution, using only one setting of the operating parameters. Finally, since it is possible that the fission fragment can produce several ions during its passage through the sample, we wished to be able to record several ion flight times for a given start signal, and we wished the deadtime to be small to permit the measurement of closely spaced signals. To meet these requirements, the flight time measuring portion of the apparatus must have a dynamic range of 0–1 ms, a measurement precision of 1 ns, the capability of recording several time intervals, a low deadtime, high linearity, and high stability. Since commercially available timing equipment cannot meet these specifications, we have designed and constructed a timing unit to meet our needs.

In this paper we describe fully the principle of operation of the timing unit, and we give general design considerations. However, we do not give complete construction details since these will depend on the particular applications.

Since our apparatus was designed and constructed, two papers describing digital timers have appeared. In one paper, Turko describes (*2*) a unit which will measure one time to a limit of 0.34 s with a resolution of 9.76 ps, and in a second paper he describes (*3*) a multiple event timer which will measure the times of 131 events with a resolution of 125 ps. The time limit is 0.33 s, and the deadtime between events is 100 ns. Both of these devices differ from ours in important characteristics, and we believe that ours is more suitable for time-of-flight mass spectrometry, which, of course, is the service for which it was designed. It can be used profitably in any kind of time-of-flight mass spectrometry wherein a well-defined start pulse is available. Examples which come to mind are laser desorption mass spectrometry and ion bombardment desorption mass spectrometry.

EXPERIMENTAL SECTION

Timing Circuitry. The essential feature of our design is to send the incoming signal pulses, such as those from the ion detector, along a delay line which at fixed distances is tapped into the inputs of fast flip-flops. When a clocking oscillator pulse occurs, the bit pattern corresponding to the presence of the signal pulses at the flip-flop inputs is recorded. If we take the period of the oscillator as T_1, we can choose the number of taps N and the time of propagation (Δt) of the signal between taps such that

$$T_1 = N(\Delta t) \tag{1}$$

The resulting N-bit word in the flip-flops represents the time of pulse(s) within the relevant oscillator period T_1. The time resolution will be Δt.

Figure 1 is a circuit diagram of half of the high-resolution portion of our time recorder. Half of the delay line is shown on the far left-hand portion of the diagram. To conserve space, we omitted the second half of the line and its identical associated circuitry from the figure. Signal pulses in the delay line within an oscillator period T_1 constitute the N bits of a word on the inputs D_0–D_3 of the F100151 flip-flop, and this word is transferred to the outputs Q_0–Q_3 of the flip-flop at the voltage edge starting the next oscillator period. The signals on Q_0–Q_3 appear on the inputs

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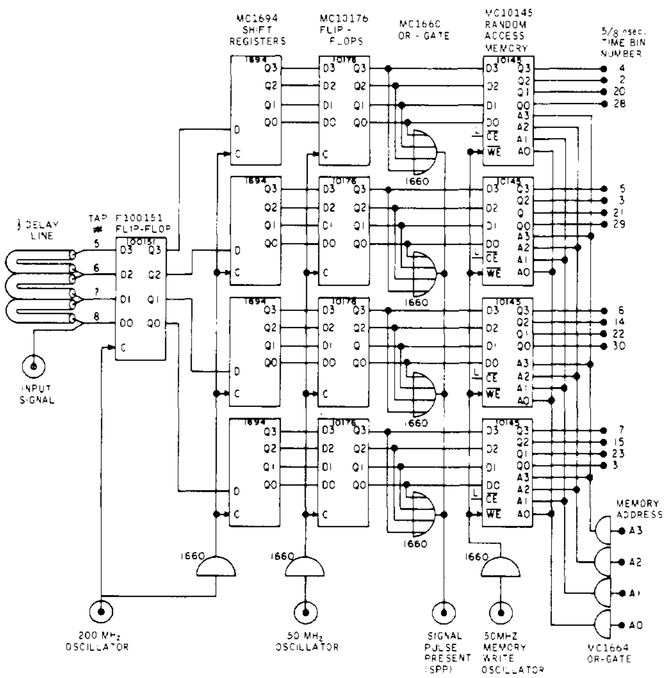


Figure 1. Half of the high-resolution portion of the time recorder.

D of the MC1694 shift registers, and they are transferred to the Q_0 locations of these shift registers at the edge starting the following oscillator period. In the following three oscillator periods, new signals appear on D and Q_0 of the shift registers, and the earlier signals are successively moved to locations Q_1–Q_3 of the shift registers. In the course of four oscillator periods a 16-bit word representing the input signals is stored in the four shift registers shown in Figure 1, which represents half of the actual circuitry. Thus in actuality a 32-bit word is assembled.

This word appears on the inputs D_0–D_3 of the MC10176 flip-flops, and the word is transferred to the outputs Q_0–Q_3 at the pulse of a second oscillator with period T_2. The second oscillator is derived from the first, and $T_2 = 4T_1$. The two oscillators are in phase. The signals on the Q_0–Q_3 outputs appear at the D_0–D_3 inputs of the MCM10145 random access memory units, and they are transferred to a memory location in the RAMs by pulses of the oscillator with period T_2. The Q_0–Q_3 outputs are sampled through the MC1660 OR-gates, and if any of the Q_0–Q_3 bits is set, the control logic causes the memory address to be advanced. If no bits are set (no input signal pulse) the memory word is written over. The MCM10145 RAMs can each accommodate 16 four-bit words, so a total of 16 32-bit words can be stored. These represent the high-resolution portions of 16 or more signal pulse times. The fact that more than 16 signal times can be stored results from the very short deadtime of the apparatus (see later), which makes possible the inclusion of the time for more than one input signal in one 32-bit word.

In our apparatus eight taps are used on the delay line, and the frequency of the first oscillator is 200 MHz (Vectron Laboratories, Norwalk, CT, Model CO-233MEH, 0.001% accuracy) corresponding to T_1 = 5 ns. Then ΔT in eq 1 is $^5/_8$ ns = 0.625 ns. These values were chosen to be in accordance with the speed characteristics of the solid-state devices used. An input flip-flop requires a set-up time, t_s, during which the signal must be present before the clock recording edge, and a hold time, t_h, during which the signal must be present after the clock edge. For the devices used here (Fairchild F100151 flip-flops) $t_s = t_h = 0.2$ ns. The outputs of the F100151 units are shifted by the fastest shift register available (Motorola MC1694), which typically requires 3 ns for a shift operation. Because of small delay skews between circuits and the need for tolerance, we decided to allow 5 ns for the shift operation, which required the choice of the 200-MHz first oscillator. Similarly allowing for tolerance in the speed characteristics of the F100151 flip-flops, a signal duration of approximately $2x(t_s + t_h) \cong 0.8$ ns is required. This in turn establishes the approximate delay time between taps, leading to our choice of eight taps and Δt = 0.625 ns. This choice gives an apparatus with an acceptable cost and degree of complexity.

A signal in the delay line must be broad enough so that it will be detected at one of the signal taps, and the minimum usable pulse width, W_{min}, is given by

$$W_{min} = t_s + t_h + \Delta t \qquad (2)$$

Using values of t_s, t_h, and Δt given above, we obtain W_{min} = 1 ns. To provide a safety factor we adjusted the pulse width to 2 ns.

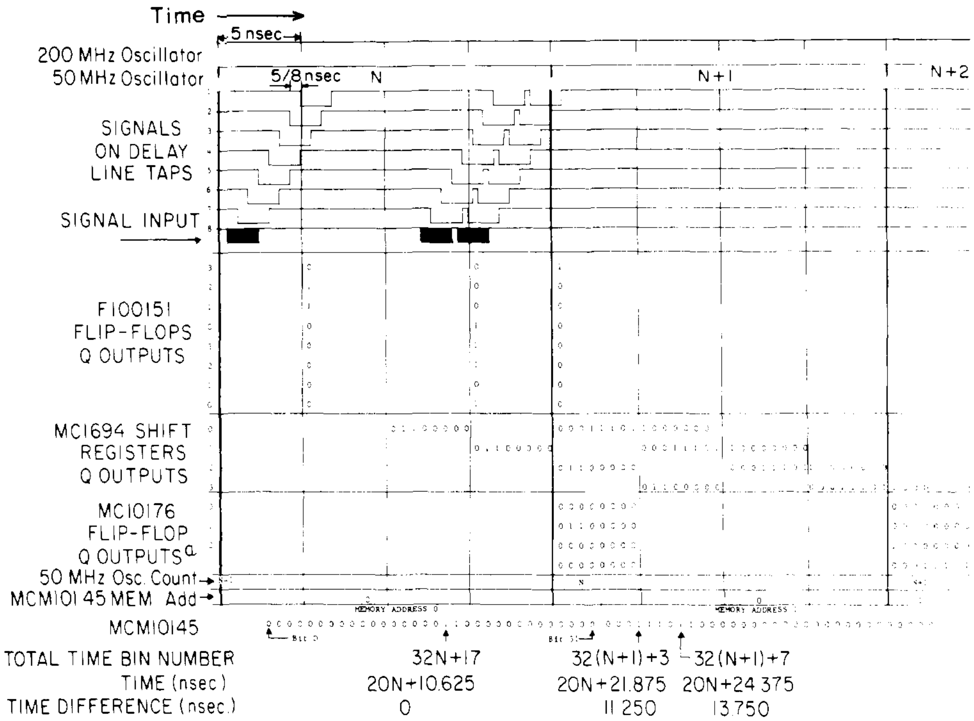
The frequency of the second oscillator was also chosen to fit the characteristics of the solid-state devices. The Motorola MC10145 memory has a worst case data set-up time of about 5 ns, a worst case hold time after writing of about 5 ns, and a worst case write pulse width of about 10 ns. This results in a maximum write cycle time of 10 ns, which is consistent with the use of a 50-MHz oscillator (period = 20 ns).

The high-resolution portion of the time recorder described above measures times up to 20 ns with an accuracy of $^5/_8$ ns. To measure longer times, we counted the 50-MHz oscillator pulses. The contents of the counter are stored in a set of MCM10145 memory units in an arrangement identical with that shown in Figure 1 except that only 4 units are used. Thus the pulse count memory contains 16 bits, which permits the storage of times up to $t = 2^{16} \times 20$ ns = 1.3 ms. The complete time for an event is comprised of the high-resolution time word from the MCM10145 memory of Figure 1 and the 16-bit pulse count word.

The essential features of the operation of the time recorder are summarized and illustrated by the time sequence and bit pattern flow depicted in Figure 2. Three signals represented by the filled pulse blocks at the signal input and delay line tap no. 8 are assumed to enter the timer after the $N - 1$ pulse of the 50-MHz oscillator. The signals are assumed to be square pulses of 2 ns duration, which is nominally the waveform and duration provided by the input clipping and shaping circuitry. This is idealized, and the actual pulse-pair separation is poorer than that represented in Figure 2. With delay line signals of 2 ns duration and delay line taps separated in time by $^5/_8$ ns, as many as three delay line taps can be spanned by a given input pulse, and correspondingly three of the inputs to the F100151 flip-flops may be set. Figure 2 shows several examples of consecutive bit sets. Since the real time of the pulse arrival in the delay line will be represented by the F100151 bit corresponding to the earliest time, the control logic searches the MCM10145 memory words for a set bit (bit = 1) preceded by a zero bit, and this bit determines the time of arrival of the pulse. For example, in memory address 0 of Figure 2, the 18th bit is ignored, and in memory address 1, the 4th and 5th bits are ignored. A set bit in the 0th location of a memory address constitutes a special case, and to deal with this, the apparatus is designed to save the signal pulse present (SPP) signal from the preceding word and use it in making the 1 preceded by a 0 evaluation for bit 0.

Readout Operation. Since we wish to measure the flight times of ions in a time-of-flight mass spectrometer, the time range of interest will vary from one experiment to the next. Therefore, our timing apparatus is equipped with two banks of 16 switches, one of which controls the start of the timing range and the other end of the range. Each switch in the bank of 16 presents a bit which is compared through exclusive-OR comparators with bits of the 50-MHz oscillator counter. Exact correspondence of the bits in the switch register with the bits in the counter produces signals which either start or stop the timing.

When the maximum time of interest is sensed, i.e., when the time scan is complete, the unit ceases to acquire data and switches to the readout mode. Gates on the input lines are closed, and the 200- and 50-MHz oscillators and 50-MHz oscillator counter are disengaged. The last address in the MCM10145 memory (Figure 1) is stored in a counter (C_D) which is set to count down. Another counter is established to count up from zero, and the value of this counter (C_U) constitutes a pointer to words in the MCM10145 memory in the subsequent readout operations. An internal 30-MHz read oscillator is activated, and it increments a five-bit counter, the binary output of which constitutes the address input of a set of four MC10164 eight-line multiplexers. The inputs of the multiplexers are connected to the locations Q_0–Q_3 of the MCM10145 memories. The incrementation of the five-bit counter thus results in a scanning of the 32 bits of the MCM10145 word addressed by the counter C_U. The connections



[a]The contents of the eight Q_0 outputs after transfer become the contents of Time Bin Numbers 24-31. Similarly $Q_1 \rightarrow$ 16-23, $Q_2 \rightarrow$ 8-15, and $Q_3 \rightarrow$ 0-7

Figure 2. Time sequence and bit pattern flow.

between the multiplexer and the MCM10145 bits are such that the MCM10145 bits are sequentially scanned from low order to high order (small time to large time). When the scanner encounters a set bit (bit = 1) preceded by a zero bit (the time of an event), the 30-MHz read oscillator is stopped, which in turn stops the incrementation of the 5-bit counter. The value of the counter comprises a binary representation of the $^5/_8$-ns time bin number; that is, it comprises the five lowest order bits of the signal pulse time word. The 16 high-order bits are contained in the MCM10145 memory associated with the 50-MHz counter. A "data ready" signal is generated, and the complete 21-bit word is transferred to a computer for permanent storage. The computer is expected to accept the data and return a "data received" signal, which turns the read oscillator back on, and the bit scanning process continues. After all 32 bits are scanned the counter C_U is incremented, and the bits of the next word in the high-resolution MCM10145 memory (Figure 1) are scanned. When counter C_U is incremented, counter C_D is decremented, and when C_D reaches zero (all words scanned), an "empty" signal is sent to the computer. The computer completes its operations and sends an "arm" signal back to the timing unit, which causes the unit to revert to the data acquisition mode (see below).

The set bit preceded by zero bit comparison referred to above is made by holding each bit being examined in a flip-flop for one oscillation of the read oscillator. Then the held bit and the next incoming bit (i.e., two adjacent bits) are evaluated in an exclusive OR-gate. An analogous procedure is used to compare the 0th bit with the SPP signal of the preceding word.

The 21-bit time words to be sent to the computer are present in the MCM10145 memory at ECL levels. Therefore they are sent to the computer through an interface circuit which contains a set of MC10125 ECL to TTL level shifters. In addition, for our mass spectrometer application of the timer, we are usually interested in knowing the differences in arrival times of the first event and subsequent events. To permit this the interface circuitry contains a set of SN7483 binary adders which can be switched into the circuit at the option of the operator. The time of the first event is inverted and then held in the adders to be deducted from all subsequent times.

The computer used in our system is a DEC PDP 11/34 with a DR11-L two 16-bit word parallel interface. Interfacing to the computer is straightforward using conventional hand-shaking routines (see above). The computer also keeps track of intensity information in the form of the number of counts in a given time range. The smaller the time range used the greater the computer memory required, and for many applications very narrow time bins are not needed. Therefore the FORTRAN program which handles the data can be directed by the operator to establish time bins of arbitrary width (greater than $^5/_8$ ns). The number of counts per bin which can be accepted is limited by the characteristics of the computer and the program. In our system the largest number of counts which can be handled is 32 000, but increasing this would be a trivial matter. Thus the dynamic range of the intensity measurement is very large.

Input Circuitry. As has been mentioned above, in ^{252}Cf mass spectrometry the two fragments produced in a nuclear fission serve different functions. One produces the ions of interest, the masses of which are to be measured by the time-of-flight technique; the other produces a pulse which serves as the starting time for measuring the flight times of the ions. We refer to the latter pulses as start pulses and the pulses produced by the ions of interest as event pulses. In our timing unit the event and start pulses are brought into the unit through separate input lines and are treated somewhat differently.

The flow of the input pulses (both start and event) is controlled by several gates. An arm signal from the computer signifying that manipulation of data from a previous operational cycle is completed accomplishes several functions: the passage of start and event pulses to the time recorder is permitted; the time recorder is turned on; and the memory address and memory write oscillators are gated on. The gate on the event pulse line also responds to the condition that it remains closed unless the time equals or exceeds that signaled by the start time switch bank. When the maximum time signaled by the end time switch register is exceeded, the actions accomplished by the arm signal are reversed. The appearance of the first start pulse after the arm signal starts the counter associated with the 50-MHz oscillator.

The times of both the start and event pulses are measured and stored with the circuitry depicted in Figure 1. However, start and event times must be distinguished from each other, and to do this the start pulse in its input line is caused to generate a start pulse tag; that is, a bit is set in a start pulse tag memory unit. The address of this tag is made to be identical with the address of the start pulse time in its memory unit, and the presence or

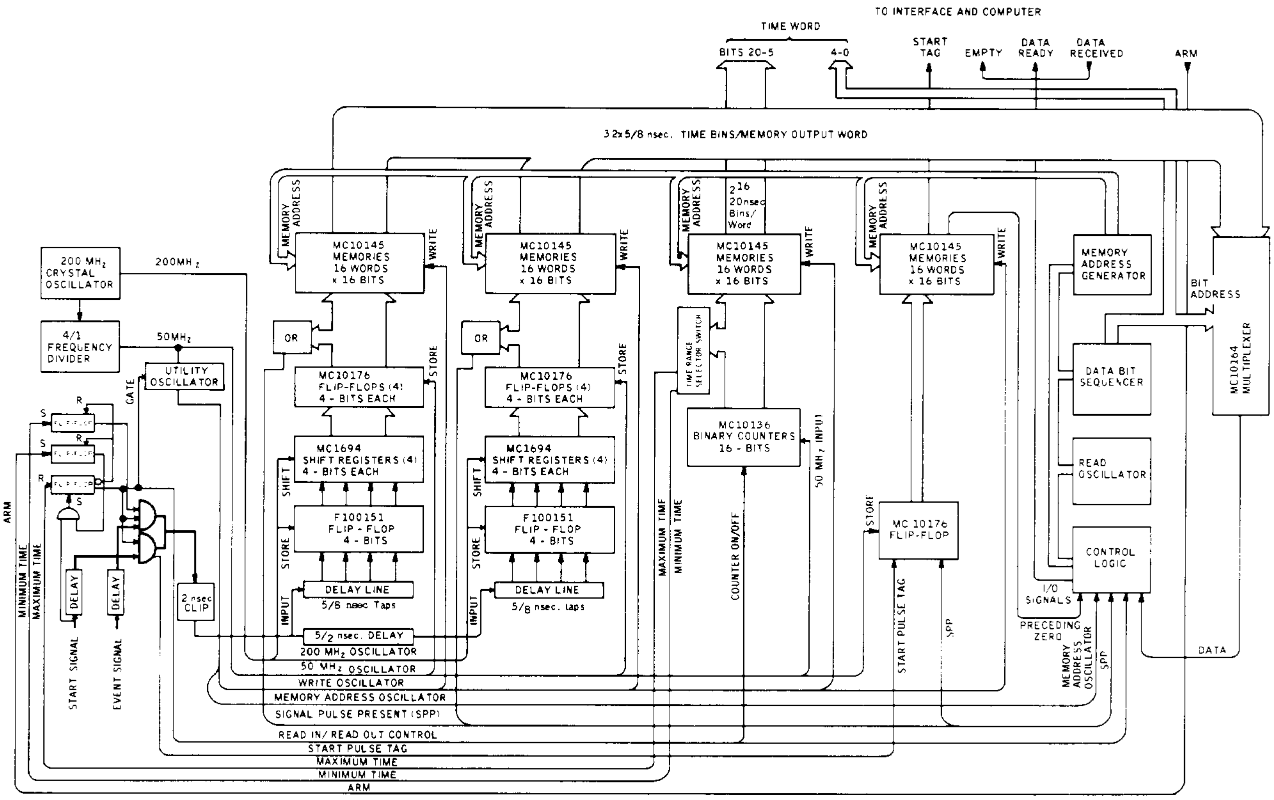


Figure 3. Summary diagram—components, interconnections, and data flow.

absence of a start pulse tag is always transmitted to the computer during the readout operation so that the computer will handle start pulse times appropriately. It must be remembered that start pulses occur continuously, and only the first one occurring between an arm signal and the maximum time signal is of value. Other start times are ignored by the computer in making the permanent storage of event times. When the subtractor facility referred to above is in operation, the time of the first start pulse after an arm signal is the one subtracted from subsequent times.

Summary Diagram. We give in Figure 3 a diagram for the complete system showing the components, their interconnections, and the data flow.

Construction Details. Motorola MECL devices are used throughout, with the exception of the TTL devices in the computer interface and the Fairchild F-100151 input flip-flops. Construction appropriate to high-speed logic devices is used. Printed circuit microstrip transmission is used for all signals on the cards associated with recording data. This requires a ground plane surface on one side of the printed circuit board and signal conductor printing on the opposite side. Runs of more than about 2 in. must be treated as transmission lines and terminated in the characteristic line impedance. All signal nets must be free of branches to avoid reflections. Specific construction details including board layout diagrams will be supplied to seriously interested readers on application to F. H. Field.

The system is modular, and simplification can be traded for performance, to some extent. If one instead of two recorder cards is used, the high-resolution part of the time word becomes 16 instead of 32 bits, and the time bin width increases to 1.25 ns. Conversely, the system could be expanded to four recorder cards to achieve $^{5}/_{16}$ ns time bin widths. A dual memory could be incorporated, so that when one memory becomes full, the other memory is selected for writing, and the first memory is read out. The system would then be capable of recording continuously.

RESULTS

Performance. Before serious design and construction was undertaken, a test was made of the basic concept of the circuit. A test apparatus consisting of a four-tap delay line, an F100151 flip-flop, and a dual pulse generator circuit was constructed. The circuit mimicked the input circuit to the F100151 flip-flop in Figure 1. A 1-ns pulse from a Hewlett-Packard Model 215 pulse generator was divided, and the separate pulses were separately delayed using EG+G Model DB-263 switchable delay boxes and General Radio Model 874 LTL delay trombones. The pulses were shaped and clipped appropriately, and one of the pulses was presented to the delay line and the F100151 flip-flop. The other activated the clock input C of the flip-flop. The time delays in the two lines were varied, which changed the differences in arrival time of the two pulses at the flip-flop. The experiment consisted of deducing the time differences in the arrival times from the signals on the Q_0–Q_3 output terminals of the F100151 and comparing these experimentally determined differences with those known to be produced in the highly accurate delay trombones. The experimental and known time differences agreed to better than 0.1 ns, which represents satisfactory performance of the flip-flop and of the general idea.

After the apparatus was constructed it was subjected to a more elaborate bench test. Once again the Hewlett-Packard Model 215 pulse generator and EG+G Model DB-263 variable delay box were used. A pulse from the generator was divided into two lines, and the pulse in one of these was delayed by differing amounts by using the variable delay box. The other pulse was delayed by a constant amount. The two pulses were recombined in one line and thereby constituted sequential pulses with a variable time separation. These were introduced into the time unit event input. A prompt pulse from the pulse generator (the sync pulse) was introduced into the start pulse input and defined the start time.

We denote the two sequential pulses entering the event input as pulse A and pulse B. The time difference between pulse B and the start pulse was constant at about 40 ns, but its absolute value was not known with high accuracy. The time difference between pulse A and the start signal was varied with the delay box, the accuracy of which is ±0.5 ns. For this pulse also absolute values were not known with high accuracy, but the delay box accuracy specification of ±0.5 ns applies to differences in delays of pulse A.

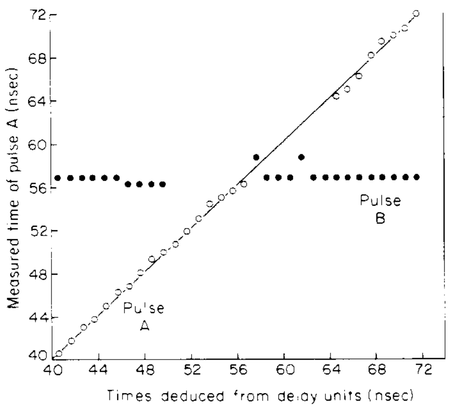


Figure 4. Test of high-resolution portion of timer—measured vs. known pulse times.

We give in Figure 4 plots of the times of pulses A and B measured by the timing unit vs. values deduced from the delaying circuitry. One first observes that the time obtained for constant pulse B was 56.875 ns for 19 individual determinations, 56.250 ns (one $^5/_8$-ns bin smaller) for 4 determinations, and 59.750 (three $^5/_8$-ns bins higher) for 2 determinations. Thus on average the precision of these measurements is within our design goal of ±1 bin ($^5/_8$ ns). The line through the points representing the times for the variable pulse A is a least-squares fit. Its slope is 0.994, which is in acceptable agreement with the expectation value of unity. The scatter of individual points around the correlation line is small, the largest deviations being on the order of one $^5/_8$-ns bin.

These results also allow one to evaluate the dead time of the apparatus. In this experiment pulse A is originally earlier than pulse B, but in successive measurements it is delayed so that it approaches, eclipses, and finally becomes later than pulse B. In the 11th measurement the time of pulse A is 50.625 ns, and it is close enough to pulse B at 56.250 or 56.675 ns to prevent the separate measurement of the time of pulse B. This represents a pulse pair resolution of about 6 ns. Pulse A appears from behind pulse B on the 25th measurement, and the pulse pair resolution deduced is 7.5 ns. As can be seen from Figure 3 the input signal is clipped to a nominal length of 2 ns, but finite rise and fall times will make the actual value longer than this. We measured an actual pulse width at half-height of 3 ns. The signals enter the timing system through two discriminators (Advanced Micro Devices AM 685), and these may contribute some spread to the input signals and produce pulse pair overlap. The observed magnitude of the pulse pair separation is in keeping with reasonable expectations from the design. Furthermore, this separation was deemed to be acceptable, and no attempts were made to maximize the separation value.

Another bench test of the completed apparatus was made, and this tested its behavior in measuring relatively long times. The test utilized a Tektronix Type 184 time mark generator feeding into a Type 101 Datapulse pulse generator. This arrangement produces a sequence of pulses with an arbitrarily selectable frequency, but one which is highly stable. The 24 h stability of the mark generator is given by the manufacturer as 3 parts in 10^6; the short-term stability is greater (perhaps 0.3 parts in 10^6). Absolute accuracy is not specified. The pulses from this generator system were introduced into the event input of the digital timing system, and an uncorrelated single pulse from a one shot was introduced into the start input of the timing system. The timing system was operated in the subtract mode, and a typical result (one of several replicates) is given in Table I.

The average of the nine Δt values is 100.0007 with a standard deviation of 0.0005. This corresponds to an integral nonlinearity of 7 parts in 10^7. We deem this performance to be quite adequate.

Table I. Digital Timing System Test, Arrival Times of a Train of Pulses[a]

pulse no.	measd time, μs	$t_{n+1} - t_n$, μs
1	99.933	
2	199.934	100.001
3	299.934	100.000
4	399.935	100.001
5	499.936	100.001
6	599.937	100.001
7	699.938	100.001
8	799.938	100.000
9	899.939	100.001
10	999.939	100.000
	av	100.0007 ± 0.0005

[a] nominal period = 100 μs.

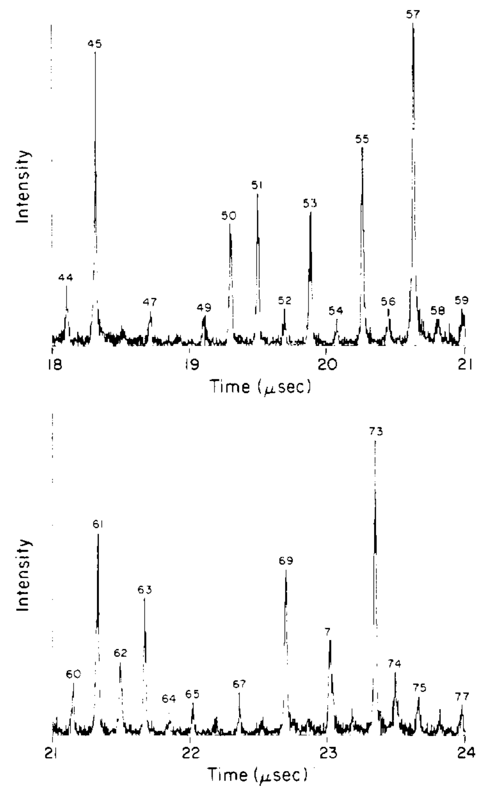


Figure 5. Portion of positive ion spectrum of sucrose.

The digital timing system has been placed in operation in our ^{252}Cf time-of-flight mass spectrometer, and satisfactory performance has been obtained. The mass spectrometer will be described elsewhere. Because the performance of the complete system depends upon many factors in addition to the performance of the timing system, overall performance cannot be looked upon as providing specific, detailed tests of the timing system. However, one can say that good performance of the timing system is required to get the results obtained.

We give in Figure 5 the portion of the positive ion spectrum of sucrose between 18 and 24 μs, which encompasses the mass range 44–77 daltons. In obtaining this spectrum the numbers of counts in time bins 3 ns wide are calculated by the computer, and these are plotted as ordinates in Figure 5. One observes the satisfactory peak shapes and the low noise between peaks.

A complete spectrum of sucrose has been obtained, but a time–intensity representation of the spectrum of the kind

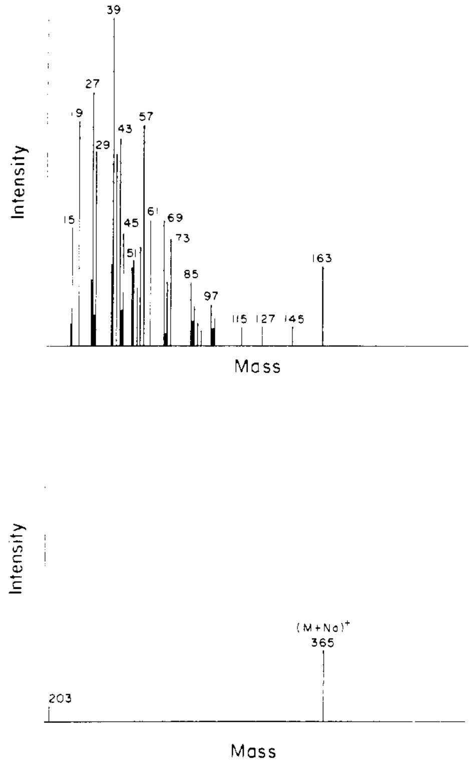


Figure 6. Complete positive ion spectrum of sucrose in histogram form.

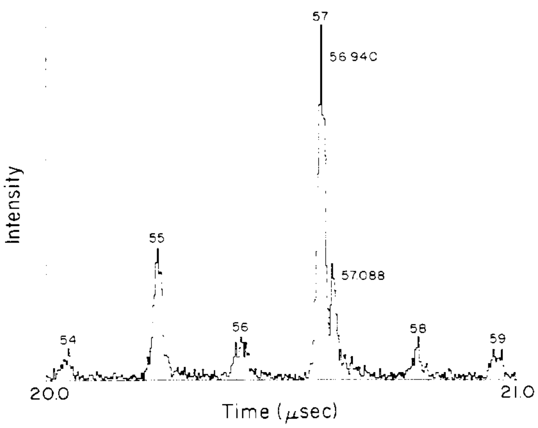


Figure 7. Portion of the position ion spectrum of alanine.

given in Figure 5 requires too much space for inclusion here. As a matter of interest the complete ^{252}Cf positive ion mass spectrum of sucrose is given in graphical histogram form in Figure 6. This spectrum has been corrected for background ions, and thus some of the ions appearing in Figure 5 are not included in Figure 6 since they are not properly part of the sucrose spectrum.

We give in Figure 7 a portion of the positive ion spectrum of alanine. The abscissa in Figure 7 is expanded three times compared with that of Figure 5, and this permits one to observe a doublet of m/z 57. The resolution represented by this doublet is about 400. The higher component of the doublet is probably $C_4H_9^+$, but we have no good idea about the identity of the very mass deficient lower component.

Finally, we give in Table II the results of six replicate determinations of the masses of the major ions from arginine.

Table II. Exact Mass Determinations from Six Replicate Spectra, Arginine Positive[a] ($C_6H_{14}N_4O_2$, mol wt 174)

m/z	exact mass	std dev	possible ion	calcd mass	Δ mass
18	18.036	0.001	NH_4^+	18.035	0.001
28	28.015	0.0004	$HC^+{=}NH$	28.019	−0.004
30	30.033	0.0004	$^+CH_2NH_2$	30.034	−0.001
41	41.024	0.002	$C_2H_3N^{+\cdot}$	41.027	−0.003
43	43.020	0.003	$C_2H_3O^+$	43.018	0.002
			$CH_3N_2^+$	43.030	−0.010
44	44.038	0.002	$CH_4N_2^+$	44.037	0.001
59	59.047	0.002	$CH_5N_3^+$	59.048	−0.001
60	60.060	0.003	$C_2H_6NO^+$	60.045	0.015
			$CH_6N_3^+$	60.056	0.004
70	70.082	0.004	$C_5H_{10}^+$	70.078	0.004
			$C_4H_8N^+$	70.066	0.016
87	87.093	0.003	$C_4H_{11}N_2^+$	87.092	0.001
			$C_5H_{11}O^+$	87.081	0.012
			$C_5H_{13}N^+$	87.105	−0.012
			$C_3H_9N_3^+$	87.080	0.013
100	100.076	0.011	$C_4H_{10}N_3^+$	100.087	−0.011
112	112.144	0.007	$C_6H_{12}N_2^+$	112.100	0.044
130	130.107	0.010	$C_5H_{14}N_4^+$	130.122	−0.015
197	197.100	0.011	$C_6H_{14}N_4O_2Na^+$	197.102	0.002

[a] Mass scale calibrated at m/z 23 and 175 $(M + 1)^+$.

These measurements were done at times differing by as much as 3 weeks. In these measurements the mass scale was calibrated at two points, namely, the ever-present Na^+ peak at m/z 22.9898 and the $(M + 1)^+$ arginine peak at m/z 175.1195. Such a two-point mass scale calibration is standard practice in our operation. We call attention first to the standard deviation of the exact experimental masses tabulated in column 3. The low values obtained bespeak a high degree of reproducibility in our measurements. The experimental exact masses in column 1 (average of the six replicates) may be compared with the calculated masses (column 5) for several possible ion compositions (column 4). We have no independent information about the compositions of the ions produced from arginine by ^{252}Cf ionization, so the conclusions to be drawn are not unequivocal. However, we think that the structures given at m/z 18, 28, 30, and 197 are quite likely (the identity of the $(M + 23)^+$ ion at m/z 197 is almost a certainty), and we think that the small Δ-mass values in column 6 for these ions represent good performance of the equipment.

To summarize, we have designed, built, and placed into operation a digital timing device with the following capabilities: (1) time bin width, $^5/_8$ ns; (2) number of time bins, $2^{21} = 2 \times 10^6$ (corresponds to 1.2 ms); (3) time span measured, switch selectable minimum and maximum times between 0 and 1.3 ms; (4) multiple stop capability, 15 event times can be measured after a given start event; (5) pulse-pair separation, 7 ns; (6) time resolution, ±1 bin ($^5/_8$ ns); (7) nonlinearity (integral), 7 parts in 10^7.

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