Analog storage register for fast transient recording

ARTICLE *in* ANALYTICAL CHEMISTRY · JANUARY 1977

Impact Factor: 5.64 · DOI: 10.1021/ac50009a013

2 AUTHORS, INCLUDING:

Chris Enke
University of New Mexico
198 PUBLICATIONS **4,582** CITATIONS

of Stewart, Beecher, and Hare (*4*) uses a reagent flow of 1.8 ml/min, or 1.08 ml/sample at the rate of 100 samples per hour. However, this moderate sample consumption is accomplished by reducing the tube diameter and increasing the pumping pressure. Stewart et al. (*4*) pointed out some of the problems associated with high pumping pressure. They have not been able to add a second reagent to the flowing stream. (Ruzicka and Hansen (*3*) showed that it is possible to add a second reagent in unsegmented flow systems that operate at low pressure.) The reaction time is also limited, both by peak spreading and by excessive pumping pressure. Stewart et al. reported that the maximum reaction time possible with their system is 120 s, as a longer reaction time would require tube lengths too long for the available pumping pressures.

Both White and Fitzgerald (*1, 2*) and Ruzicka and Hansen (*3*) developed systems with low pumping pressure, but the reagent consumption was large in both cases. The method of analysis used by White and Fitzgerald was photochemical, and the reagent can be reused (*1*). Ruzicka and Hansen employed relatively inexpensive reagents. When the reagents are inexpensive and the sample sizes are not a limitation, unsegmented continuous flow becomes more attractive.

Unsegmented continuous flow appears to have some advantages when it can be used. Segmented continuous flow systems take some time to reach a steady state, especially when the reaction times and tube lengths are long. As was noted by Ruzicka and Hansen (*3*), the unsegmented streams reach stable flow almost immediately, and the system can start doing analyses virtually as soon as the pump is started.

ACKNOWLEDGMENT

Discussions with Robert Stoy have been of great help in the preparation of this publication.

LITERATURE CITED

(1) V. R. White and J. M. Fitzgerald, *Anal. Chem.*, **44**, 1267 (1972).
(2) V. R. White and J. M. Fitzgerald, *Anal. Chem.*, **47**, 903 (1975).
(3) J. Ruzicka and E. H. Hansen, *Anal. Chim. Acta*, **78**, 145 (1975).
(4) K. K. Stewart, G. R. Beecher, and P. E. Hare, *Anal. Biochem.*, **70**, 167 (1976).
(5) D. H. Spackman, W. H. Stein, and S. Moore, *Anal. Chem.*, **30**, 1190 (1958).
(6) J. C. Sternberg and R. E. Poulson, *Anal. Chem.*, **36**, 1492 (1964).
(7) J. C. Giddings, "Dynamics of Chromatography, Part I. Principles and Theory", Marcel Dekker, New York, 1965, pp 219 ff.
(8) V. Pretorius and T. W. Smuts, *Anal. Chem.*, **38**, 274 (1966).
(9) L. T. Skeggs, *Am. J. Clin. Pathol.*, **28**, 311 (1957).
(10) D. A. Lane and J. A. Sirs, *J. Phys. E*, **7**, 51 (1974).
(11) J. Ruzicka and J. W. B. Stewart, *Anal. Chim. Acta*, **79**, 79 (1975).
(12) Industrial Method No. 94-70W/B, "Orthophosphate in Water and Wastewater", Revised Jan. 1976, Technicon Industrial Systems, Tarrytown, N.Y. 10591.

RECEIVED for review August 5, 1976. Accepted October 25, 1976.

Analog Storage Register for Fast Transient Recording

T. A. Last and C. G. Enke*

Department of Chemistry, Michigan State University, East Lansing, Mich. 48824

A fast transient recorder, employing a temporary analog storage register was developed. This type of transient recorder can provide a significantly better price/performance ratio than the more conventional digital types over a sampling rate range from 0.1 to 10 MHz. The implementation of the analog storage device is discussed, and the performance of the transient recording system is demonstrated. Linearity and accuracy of better than 1% were obtained at recording rates up to 10 MHz.

There are many measurements (e.g., kinetics studies by perturbation techniques (*1*)) which require the ability to record the amplitude vs. time function of a short-lived and rapidly varying signal. The most popular solution to this problem has been the "fast digitizer" (*2*) which converts the incoming analog signal amplitude into a digital data word at regular intervals and then stores the digital words from successive conversions in a high speed memory. This produces a digital record of the signal amplitude at a number of sequential points in time. While this digital recording technique can be inexpensively implemented at moderate data rates (up to about 50 KHz), the cost increases rapidly as the speed requirements for the analog-to-digital converter (ADC) and digital memory become more demanding.

One way to eliminate the need for these high speed components while maintaining a high recording rate capability is through the use of a temporary analog storage register which can read data in at a high rate and read data out at a lower rate. A moderately fast data acquisition system is then adequate to handle the readout rate from the analog storage register. In fact, the output rate from the analog storage register can be made slow enough to eliminate the need for any digital storage other than the computer memory in a computer-based acquisition system. These two recording schemes are contrasted in Figure 1. The transient waveform is clocked very rapidly into the analog memory and then clocked out at a rate compatible with an ordinary ADC. The converted data can then be sent to the computer, at software data transfer rates, where it is stored for later analysis. Since the analog storage register is comparatively inexpensive, the cost of the analog storage transient recorder can be significantly less than a digital storage recorder which has the same recording speed.

A transient recorder developed in our laboratory, which utilizes a Reticon SAD 100 serial analog delay element is shown in Figure 2. The timing section of the recorder contains a crystal oscillator which is divided to obtain selectable, accurate data clocking rates up to 10 MHz (the analog register's approximate maximum data rate). This section produces the frequency shifting necessary for changing from the fast clocking rate (while the data are being stored) to the slow rate (while the data are being read out).

The Reticon SAD 100 consists of 100 sequentially addressable storage cells contained on a single monolithic integrated circuit. Functionally, this is implemented with 2 banks of 50 cells each, which are alternately accessed to increase the storage rate. Each storage cell consists of a read in switch (FET), a read out switch, and a storage capacitor. As the ring counter in each bank is sequenced through its possible states, the nth cell is addressed for read in while the $(n + 1)$th cell is

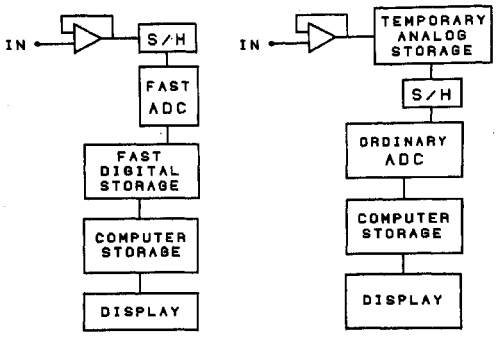

Figure 1. Comparison of transient recorder employing a temporary analog storage register with one which uses all digital storage

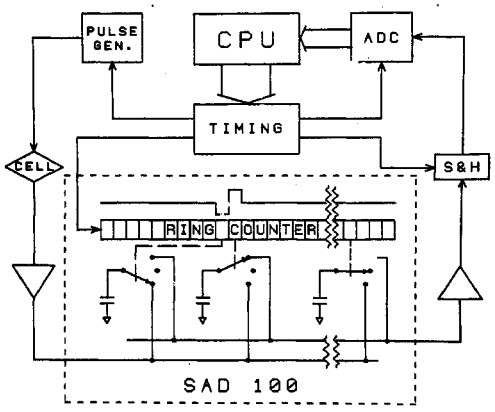

Figure 2. Block diagram of a fast transient recorder which employs the SAD 100 (serial analog delay element)

simultaneously addressed for read out. In this manner, data clocked in at any instant will appear at the output 98 clock cycles later. Thus 98 data points can be acquired at a fast rate (up to 10 MHz or 100 ns per data point) and then clocked out to the ADC at the appropriate speed while still acquiring data at this slower speed. This is particularly useful for transients of the decaying exponential shape. A primary application of this transient recording system in our laboratory is the study of the transient voltage response produced by pulsing bilipid layer membranes with a brief current pulse. This experiment produces a decaying exponential voltage transient with a time constant ranging from several microseconds to a few milliseconds. The bandwidth of this type of signal is continuously decreasing and the early points must be recorded rapidly whereas the later points can be recorded much more slowly. More SAD 100's could be combined to increase the memory size if desired. Data can be stored in the analog memory for times up to 40 ms with less than 1% retention loss (*3*). This allows a data acquisition time as long as 400 μs per point for the digitization and storage of the analog-stored data. There are a number of other analog storage devices available (although the SAD 100 is at present the fastest), some with up to 1024 storage cells, and others with up to 5-s retention time. An excellent review of the types of devices currently available, is given in Reference 4.

The Timing Circuit. One important consideration in this scheme of transient recording is the necessity to be able to change clocking rates without losing the timing integrity (the accuracy of the time of each data point) of the experiment. While recording the transient waveform it is necessary to clock the analog storage register very rapidly. However the recorded data must necessarily be clocked out for digital conversion at some rate slower than the maximum conversion rate. After this clocking frequency shift has been made, the analog register continues to collect data at the slower rate. In order for the time correlation of the data collected at the two rates to be accurate, the shift from the fast clock rate to the slower clock rate must be made in such a way as to avoid the occurrence of any spurious clock transitions. A circuit which controls the timing of the experiment in this manner is shown in schematic form in Figure 3. The operation of the circuit is as follows: the crystal controlled oscillator frequency (10 MHz) is divided by the synchronous counter to give selectable data in (multiplexer 1) and data out (multiplexer 2) clocking rates with the proper phase relationship. These frequencies are pre-selected by the computer. The number of fast data points (up to 98) is pre-set in the 7 bit up/down counter. Prior to the start of the experiment, oscillator gate 1 inhibits clocking the up/down counter, and the fast clocking rate is selected (FF2, $\bar{Q} = 0$). The analog storage register is in its fast record mode and cycling through its storage cells. This scheme allows a pre-trigger record feature since, in the waiting state, the analog register is continuously recording at the fast rate. The function of the oscillator gate is to allow only full clock cycles to pass through the gate when it is enabled or inhibited. A detailed description of the operation of the oscillator gate is given in Reference 5. When the transient recorder is armed (FN2 or Manual Start), output Q of FF5 goes to "1" which enables the oscillator gate, and on the next rising clock edge (out of osc. gate 1) the experiment stimulator is triggered by FF6, and the up/down counter begins counting off data points. When the counter reaches 0, the data clock is inhibited ($\bar{Q}$ of FF2 $\rightarrow$ 1) while the synchronous counter is reset, the clocking rate is shifted to the slower rate (FF1, $\bar{Q} = 0$) and the sample and hold (S&H) and ADC convert command are enabled. On the clock cycles which follow, data will continue to be collected at the slow rate, while data already collected will be shifted out to the ADC. This triggering approach is useful for those cases where the transient is induced by the recording instrument. There are many cases, however, where it is desirable to record an event which occurs spontaneously (e.g., the decay of a nuclear particle). In those cases it is necessary to trigger the transient recorder with the event. This could be implemented with the timing circuit by replacing FN 2 (computer start) with a trigger pulse derived from some feature of the transient waveform (e.g., a Schmidt trigger with a variable voltage level could signal the leading edge of a voltage transient). This trigger pulse would again arm the transient recorder and it would continue on as described above.

The Analog Register. The schematic diagram for the circuit which controls the SAD 100 appears in Figure 4. The clock signal from the timing section is divided by the three Schottky flip-flops to produce a quadrature clock capable of interleaving the twin banks (Rows A&B) of storage cells within the SAD 100. The 3-input NAND gate ensures that the phasing of the quadrature clock remains proper.

Since the SAD 100 is a MOS device, level shifters must be employed in order to interface to TTL signals. This is accomplished by the two MH0026 drivers, and also the Zener diode, N-channel MOSFET (SD 210) combinations.

The analog signal is amplified by the LH0032 FET input operational amplifier (National Semiconductor). This must be included to avoid loading the signal source, since the input impedance of the SAD 100 is only a few thousand ohms. In our primary application, the amplifier resides at the experiment, and a buffer amplifier (National Semiconductor LH0063) drives the signal along 50-Ω coaxial cable to the SAD 100.

The analog signal is stored in the internal storage cells of the SAD 100 as a quantity of electrical charge. Functionally these cells consist of the capacitance of reverse biased pn junctions within the SAD 100. The typical capacitance of a cell is 1.2 pf, which yields a maximum stored charge of about 5 pc. Therefore the output of the SAD 100 must be connected to an

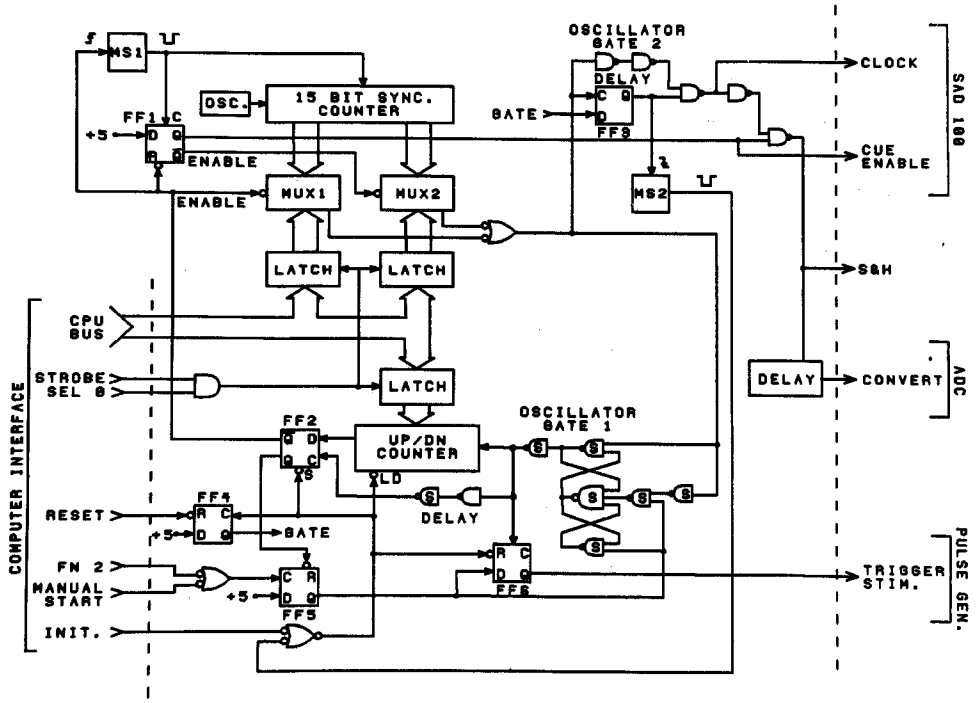

Figure 3. Schematic of the circuit which controls the timing for data collection and clocking for the analog storage register

Components: FF1–3, 74S74; FF4–6, 7474; MS1–2, 74121; MUX1–2, 74151; SYNC. Counter, 74161; UP/DN Counter, 74192; Latches, 7475; all gates labeled "S" are Schottky TTL

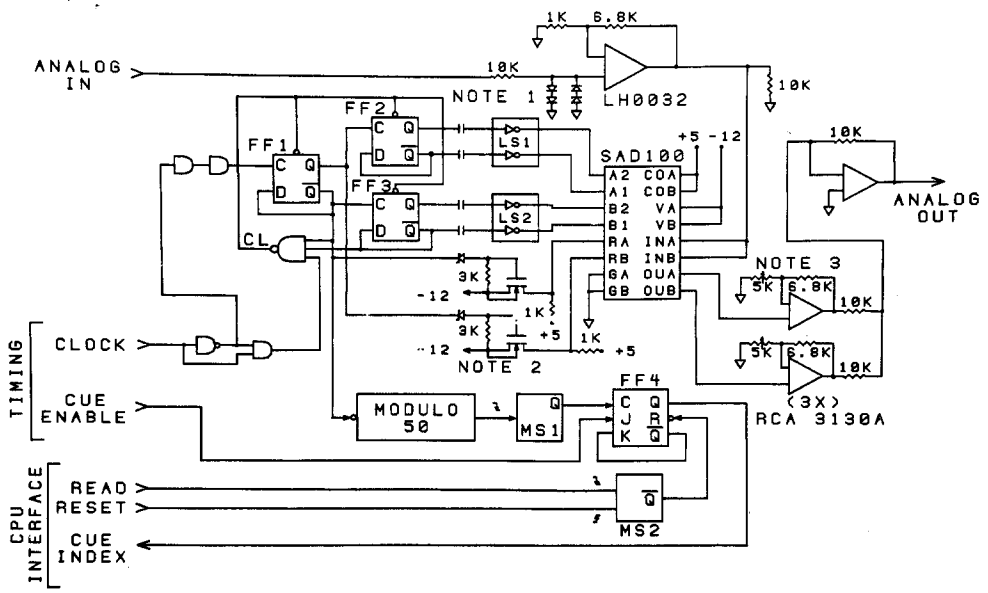

Figure 4. Schematic of circuitry employed for tending the SAD 100

Components: FF1–3, 74S74; FF4, 7476; LS1–2, MH0026; MS1–2, 74121; MODULO 50 Counter, 7490 (NOTE 1: Protection Diodes 1N914, FD300 in series; NOTE 2: MOSFET's are SD210, Zener diodes are 11 V; NOTE 3: 5K Trimpots are for gain balance)

extremely high input impedance device. Low lead capacitance is also an important consideration.

The analog outputs of the SAD 100 are connected to high input impedance (FET) operational amplifiers (RCA 3130 A) placed as close as possible to the SAD 100 in order to keep the leads short (This minimizes capacitance and stray signal pickup.) The two alternating storage banks are then summed together to reproduce the original input voltage signal. This last part is possible because the SAD 100 internally shunts one output line to ground while the other is active. The output signal should be sampled and held, because even with the high input impedance (typically 1.5 TΩ) of the RCA 3130 A, a significant droop would occur during the readout time at the slow output rate.

A circuit card (SC 100) which is similar to the circuit shown in Figure 4 is available from Reticon Corporation. The circuit card was found to be inappropriate for this application, however, in two respects. First, it is necessary to accurately control the clocking rate of data into the SAD 100. The on-board RC oscillator of the SC 100 is not sufficiently accurate and is not readily computer controlled. The second problem arises in the output buffering of the charge contained in the SAD 100. The SC 100 uses discrete MOSFET transistor charge amplifiers which are necessarily ac coupled to the output amplifier. The ac coupling causes all signals which are not symmetrical about 0 volts to be distorted.

Performance. The performance of the transient recording system is illustrated in the next five figures. These figures

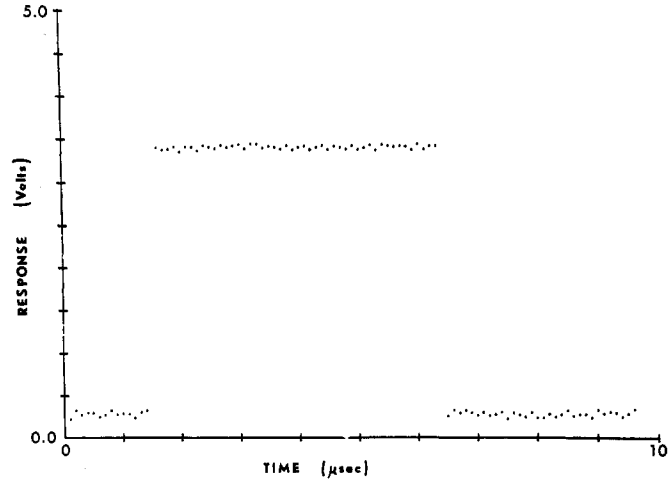

Figure 5. Response of transient recording system of 3 V at 100 kHz square wave. Data collection rate; 10 MHz

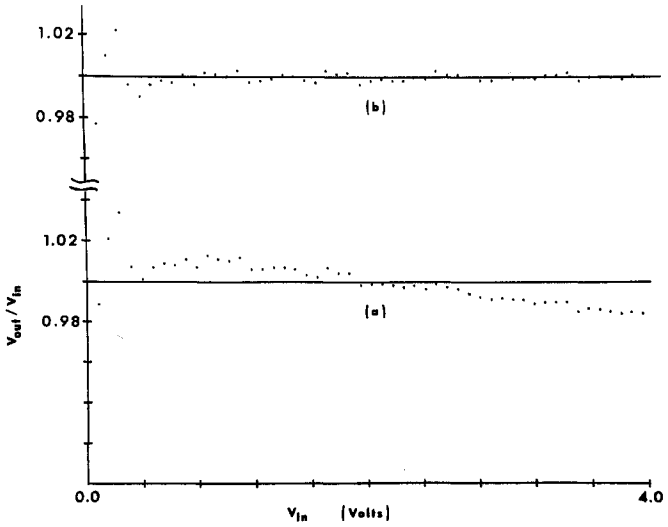

Figure 6. Linearity of the transient recording system over the range of 0 to 4 volts

(a) Plot of V_{out}/V_{in} vs. V_{in}, data collection rate = 5 MHz; (b) corrected data

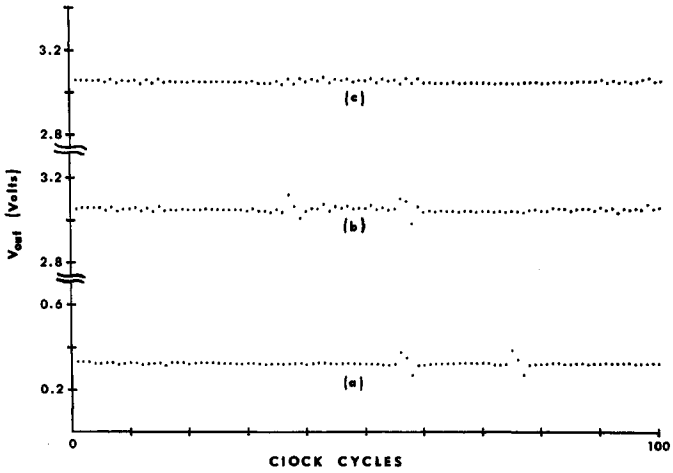

Figure 7. Signal-to-noise ratio of data collected at 10 MHz

(a) Result of 100 averages made on a low baseline voltage; (b) 100 data points (one shot) collected with a constant input voltage of ~3.0 volts, (c) result of baseline subtraction on data represented in (b)

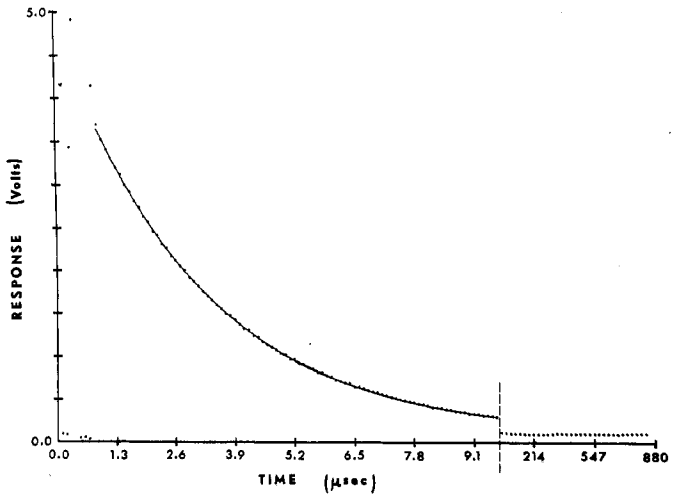

Figure 8. Recorded decaying exponential transient

Transient was produced by applying a 200-ns current pulse to a resistor and capacitor in parallel. Data were collected at 10 MHz and converted (analog to digital) at 39 kHz. RC (theoretical) = (3.000 ± 0.015) × 10^{-6} s, RC (measured) = (3.028 ± 0.004) × 10^{-6} s. Solid line represents weighted linear least squares fit to data. Discontinuity is due to data rate change. Slow data rate was used to obtain baseline

demonstrate the rise time, linearity, signal-to-noise ratio, and accuracy of the system. Figure 5 shows the response of the transient recorder to a 100-kHz, 3-V square wave. The data were clocked in at 10 MHz and then clocked out to the ADC at about 39 kHz. It can be seen from the figure that the system responds to voltage steps within 2 data points. Furthermore it is apparent that no significant bleeding between adjacent cells occurs while the information is stored in the SAD 100. If bleeding were occurring, it would manifest itself in a round-off at the voltage steps.

The linearity of the system is shown in Figure 6. The SAD 100 is specified by the manufacturer (*3*) to be linear over a range of 0–4 volts in its present configuration. The response of the recording system over this range, is demonstrated by plotting V_{out}/V_{in} vs. V_{in} (Figure 6a). It is clear from the figure that an inherent nonlinearity of 2–3% is present, and that it is a systematic nonlinearity. This nonlinearity increases with decreasing readout clock rate and is probably due to the "droop" of the Reticon storage cells. This effect would be essentially constant, however if the readout rate remains constant, and the data taking rate is greater than the readout rate by several-fold. (This is always the case for fast transients.) In the case stated, this nonlinearity would remain constant and could be corrected numerically. Figure 6b shows the result of a computer correction made on the data by performing a 6th order polynomial fit, and then using the coefficients to correct the data. These coefficients can be stored and used to correct subsequent data sets. The scatter in Figure 6b has been reduced to about 0.5–1%.

Baseline Correction. Early in the development of this system, it was noticed that a problem of glitches existed in the output of the SAD 100. Two spurious voltage spikes appeared at the output, and they appeared once for each 100 data points collected. This noise is believed to be due to phasing differences which occur during the reset cycle of the ring counters within the SAD 100. This explanation has been corroborated by the manufacturer.

Since the noise spikes appeared to be a characteristic of the analog storage register, it seemed that the best way to eliminate them was to numerically subtract them out in the data processing routine. This was accomplished by collecting a baseline scan and subtracting this set point by point from the data scan. This scheme requires the knowledge of when the noise spikes occur in the data stream, however, and to this end the cue index circuit (lower part of Figure 4) and a second

oscillator gate (upper right hand corner of Figure 3) were added. Prior to the addition of oscillator gate 2, it was observed that upon reset of the transient recorder (i.e., change back to fast recording rate), a short burst of pulses occurred, which was capable of changing the time relationship between the two noise spikes within the SAD 100 (i.e., changing the relative states of the two internal ring counters). The oscillator gate (gate 2) now ensures that no clock pulses can leave the timing circuit during the reset cycle. The cue index circuit, composed of the modulo-50 counter and flag circuitry, generates a pulse once per 100 clock cycles of the SAD 100. Since the noise spikes from the SAD 100 are generated by a particular state of the ring counters internal to the device, their time relationship to the cue index pulse will remain constant while the system is operating. This time relationship is not reproducible over successive power up cycles of the system however, so it is necessary to collect a baseline scan each time the system is powered up, and then use this baseline scan to correct the data scans which follow.

Figure 7 shows the results of a baseline subtraction made on a data set consisting of 100 data points collected at 10 MHz from a constant input voltage (~3V). The bottom trace (a) represents 100 averages of a low baseline voltage. The middle trace (b) is the single shot of data, and the upper trace (c) is the result of the baseline correction. The signal-to-noise (S/N) ratio of the uncorrected data scan is 210 and the S/N ratio of the baseline corrected scan is 378. This corresponds to nearly 9 bits of resolution. The S/N ratios were obtained by dividing the average of the data set by its standard deviation.

Transient Recording. The accuracy of the transient recorder in a real application is illustrated in Figure 8. The transient resulting from an RC decay was recorded at 10 MHz. The transient was produced by applying a 200-ns current pulse to the parallel combination of a 300-Ω, 0.01% resistor and a 0.01-μF, 0.5% capacitor and monitoring the voltage decay. A weighted least squares fit was performed on the linearized data and the slope of the fit compared to the RC time constant for the components mentioned. It is seen from the figure that the measured result is in good agreement with the theoretical value.

The cost of the SAD 100 is $100. The total parts cost of the transient recording system as described (not including computer and peripherals) was under $1000. The performance of the system with respect to speed and accuracy is certainly competitive with commercial transient recorders costing much more. The combination of cost and performance makes this method of transient recording very appealing, and the potential applications for this technique should increase still further as MOS monolithic technology expands.

LITERATURE CITED

(1) J. E. Stewart, *Am. Lab.*, No. 11, 91–101 (1973).
(2) W. P. Cargile and B. J. Moore, *Res. Develop.*, **24**, 32–35 (1973).
(3) Data Sheets for SAD 100, obtained (on request) from Reticon Corp., 910 Benicia Ave., Sunnyvale, Calif. 94086.
(4) G. Horlick, *Anal. Chem.*, **48**, 783A–787A (1976).
(5) H. Malmstadt, and C. G. Enke, "Digital Electronics for Scientists", W. A. Benjamin, New York, 1969, p 226.

RECEIVED for review June 25, 1976. Accepted October 1, 1976. The authors are grateful to Michigan State University for the Quill Fellowship received by one of us (T.A.L.). This paper was presented at the second annual meeting of the Federation of Analytical Chemistry and Spectroscopy Societies.

Loss of Carbon-14 and Mercury-203 Labeled Methylmercury from Various Solutions

Kenneth R. Olson[1]

Department of Environmental Physiology, Rutgers University—The State University of New Jersey, New Brunswick, N.J. 08903

Disappearance of methylmercury and the lability of the methylmercury bond during volatilization was studied by the incubation of submicromolar concentrations of $^{14}CH_3HgCl$ and $CH_3{}^{203}HgCl$ for 96 h in solutions routinely encountered in environmental and laboratory situations. Media with high ionic strength, 0.5 M NaCl and artificial sea water lost more mercury than deionized water, tap water, water from fish holding tanks, basic and acidic solutions, and phosphate buffered saline. Loss from the former solutions appears to be a continuous process while occurring in the first few hours in the latter. Total loss did not exceed 20% in any experiment and was due primarily to mercury in the inorganic form.

Loss of inorganic mercury(II) from dilute aqueous salt solutions has been observed by numerous investigators (*1–5*), and, although there is somewhat less evidence, it appears that monomethylmercury is also lost from aqueous solutions (*6, 7*).

Burrows and Krenkel (*7*) aerated submicromolar methylmercury ^{203}Hg solutions for 20 h and demonstrated considerable variation in loss of isotope depending on the nature of the aqueous media employed. Under these conditions 91% of the radioactivity was lost when methylmercury was placed in deionized tap water, 5% when in Nashville tap water, and 30% if the aforementioned tap water was charcoal filtered. Water collected from the shallows of a reservoir lost around 15% of the isotope. The authors suggest that the loss of mercury from the above solutions is probably in the methylated form although studies have not been done to verify this point.

The purpose of the present investigation is to pursue the work of Burrows and Krenkel with respect to 1) characterization of aqueous solutions from which methylmercury can be lost and 2) the lability of the methyl–mercury bond during mercury loss from various aqueous solvents.

EXPERIMENTAL

Glass staining dishes 94 × 70 × 55 mm (L × W × H) were used for the aeration vessels. It was thought that use of conventional aquarium air stones for aeration might provide a relatively large surface area for adsorption of the methylmercury so to prevent this possibility all aeration was with plastic tubing heat-sealed on one end with a hemostat and perforated 20 times with a 22-gauge stainless steel needle.

[1] Present address, Indiana University School of Medicine, South Bend Center for Medical Education, Medical Science Building, University of Notre Dame, Notre Dame, Ind. 46556.