High-speed device for synchronization of natural-drop experiments with a dropping mercury electrode

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tribution to less than 2%, at which point it is neglected.

The use of ^{24}Na, ^{28}Al, ^{31}Si, and ^{46}Sc for the determination of Mg, Si, P and Ti, respectively, is shown to be strongly influenced by one or more interfering reactions (production ratios <1). In order to use these four (n,p) reactions, one must have prior knowledge of the concentration of Al, Na, Si, and Sc to properly correct for the (n,γ) contribution. The ^{27}Al-(n,p)^{27}Mg reaction could be used for Al determination with minimal (n,γ) correction; however, the precision achieved is not comparable to that using thermal neutrons and conventional (n,γ) activation for Al. Even though analytical data on these four elements can be resolved from among the competing reactions with a sacrifice of precision, Si, Al, and Ti can be more easily measured by other (n,p) or (n,γ) reactions. Neither (n,γ) nor (n,p) methods are particularly sensitive for Mg determination and nonnuclear techniques are preferred.

Epithermal activation via (n,p) reactions provides an alternative, although less sensitive, method for the determination of Fe, Al, Na, Ni, and F. The preferred techniques are probably thermal neutron activation for the first three elements, atomic absorption for Ni, and ion selective electrode for F. Titanium and Si can be measured much more sensitively using the (n,p) reaction than by thermal neutron activation.

ACKNOWLEDGMENT

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High-Speed Device for Synchronization of Natural-Drop Experiments with a Dropping Mercury Electrode

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There are many types of experiments performed with dropping mercury electrodes (DME) in which measurements must be made at times that are well defined relative to the birth of the drop. The simplest method for measurement synchronization is to dislodge the drop forcibly and simultaneously trigger a timing circuit. However, mechanical drop dislodgment may cause significant disturbance of polarographic diffusion profiles in the growing drop, particularly at subsecond current sampling times (1). An alternative approach is to detect the birth of a new drop following natural gravitational drop fall. Such drop-fall detectors also enable natural drop times to be determined, providing a simple route to the interfacial tension (2).

We have been investigating dc polarographic current–time curves at short times (0.01–1 s) following drop birth to evaluate rapid dc polarography (1, 3) as a method for monitoring the kinetics of electrode reactions (4, 5). For this purpose, as well as other applications where accurate knowledge of the drop time and/or electrode area is required, it is desirable to detect the time of consecutive natural drop fall with millisecond accuracy and in a manner which is compatible with potentiostatic circuitry and automated data acquisition by a laboratory microcomputer.

Although a sizable number of detection techniques have been reported (for example, see citations in refs. 6 and 7), few fulfil the above criteria. Nearly all use either a superimposed ac voltage or light as probes, although an FM transmitter and receiver have been employed to exploit the behavior of a DME as an antenna (8). While the optical detectors (7) offer the

advantage of requiring no electrical connection with the cell, they are subject to serious errors of up to 100 ms (4). A number of the ac devices described either are not compatible with conventional potentiostat-based instrumentation (e.g., ref. 9), have response times on the order of tens of milliseconds (10), or continuously impose an undesirable ac perturbation on the cell and require remote activation and disabling because of a limited noise immunity (6). A recently reported technique (11) for making drop time measurements averaged over successive drops is simple in concept but requires adjustment as the cell current is changed, and in the vicinity of the potential of zero charge (pzc) it relies on stray impurity currents. Since these limitations render the previously described detectors inadequate for our purposes, we have developed a faster, more sensitive and versatile device which is described here.

PRINCIPLES OF OPERATION

Operation of the detector can be understood with reference to the block diagram (Figure 1) and schematic (Figure 2). Late in the drop life, the monostable which produces the delay for measurement of the dc current (D) returns to its stable state and closes the analog switch. An ac perturbation of 10 mV peak-to-peak at 100 kHz is imposed on the cell, and the resulting ac component of the cell current is detected by a tuned amplifier (A). When the electrode area is large enough so that the magnitude of the ac current exceeds the threshold selected by the potentiometer, the logic-level output of the level detector (B) will change states at the frequency of the
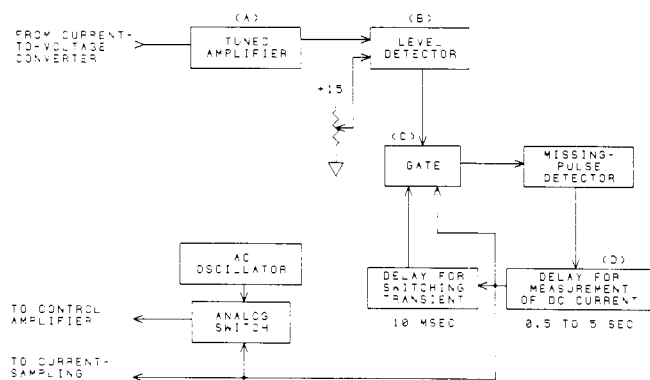
Figure 1. Block diagram of drop-fall detector

ac source and activate the missing-pulse detector after a delay to allow for switching transients. The precipitous decrease in electrode area concomitant with drop fall causes the tuned amplifier output to remain below the threshold throughout several ac cycles, long enough for detection of the missing transitions in the level-detector output. Within 100 to 200 μs of the fall of the drop, the ac source is disconnected from the potentiostat so that dc measurements can be made. The missing-pulse detector input is inhibited by the gate (C) to prevent noise transients from retriggering the detector, and a signal is sent to the current-sampling circuitry.

The time interval between the fall of the drop and its detection is due to three causes. First, at potentials away from the pzc, the potentiostat must supply charging current to the nascent drop. The resultant current spike (typically 50 μs)
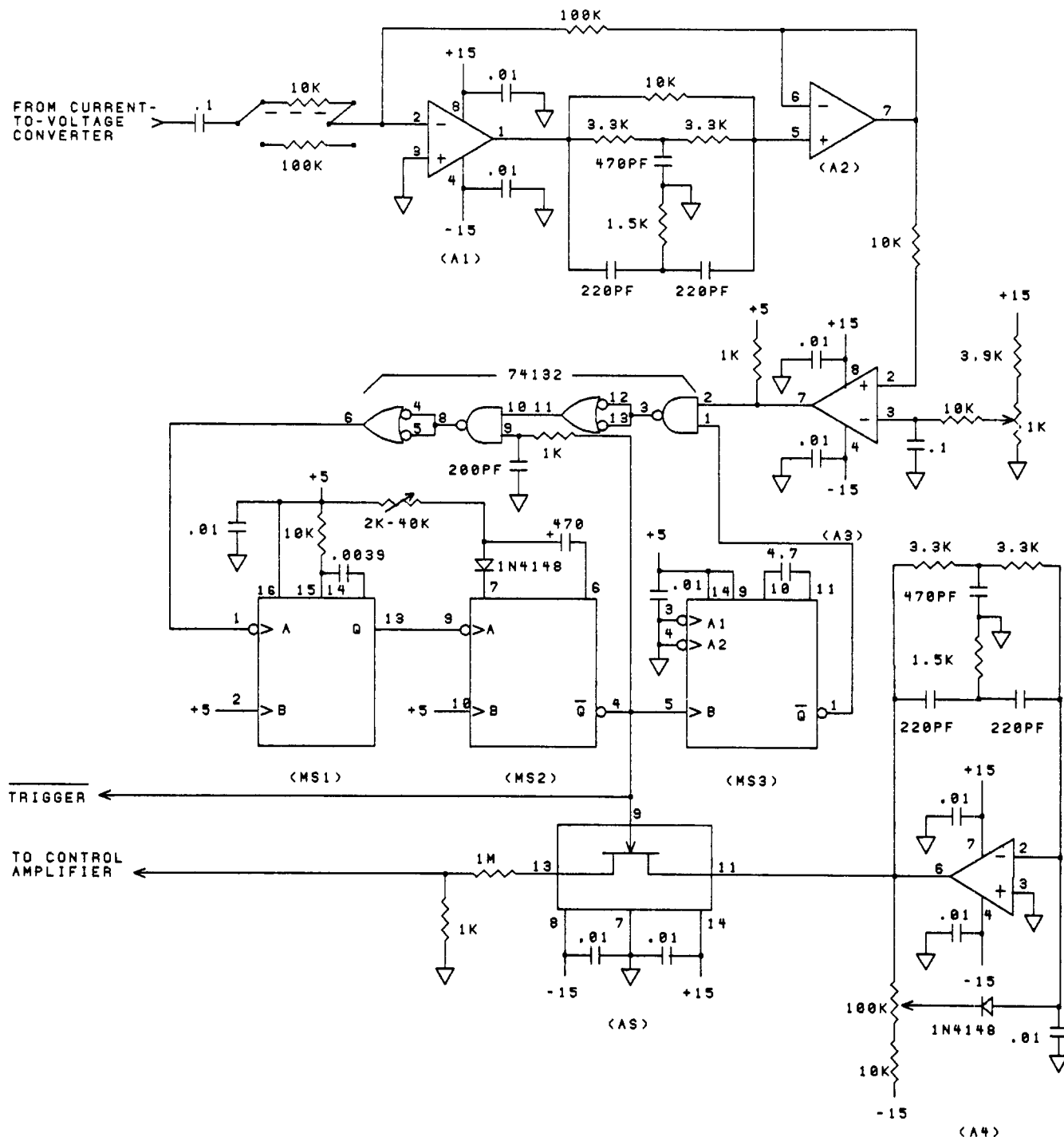

Figure 2. Schematic diagram. A1, A2, National LF353N; A3, National LM311N; A4, Signetics NE535V; MS1, MS2, SN74123; MS3, SN74121; AS, Siliconix DG300CJ

contains frequency components which can be detected by the tuned amplifier and which may keep the amplifier output above the level-detector threshold for a brief time after the drop has fallen. Second, the tuned amplifier must respond to the sudden change at its input with a deliberately constrained frequency response. Several periods of oscillation at the center frequency are required to accomplish this. Third, a full period (15 to 20 μs) of the missing-pulse detection monostable must elapse between the last output transition of the level detector and the production of the trigger signal for the current-sampling circuitry. Finally, noise in the current-to-voltage converter whose power spectrum overlaps the frequency range of the tuned amplifier can delay detection of drop-fall a few additional ac cycles.

The drop-fall detector operates reliably even in noisy environments provided the potentiostat employed has sufficient response at the frequency of the ac perturbation. Although we have chosen a frequency of 100 kHz, the detector is suitable for slower potentiostats providing that a lower frequency is selected, albeit with some lengthening in drop-detection time. This modification needs to be performed only once and is accomplished by varying the passive components in the twin-T networks around amplifiers A1 and A4 (12) and the timing capacitor on MS1. A single selection of the suitable gain (two are available) for the tuned amplifier and of a threshold level appropriate to the current-to-voltage converter setting, to the electrode capacitance, and to the cell resistance generally suffices over a wide potential range (2 V or more) for a given set of cell conditions. Since no further adjustments are required, this circuit is very useful as a trigger device for automated instruments, especially those under the control of a laboratory computer. The circuit's independent nature allows the computer to perform lower priority tasks between measurements, instead of requiring that the processor continually monitor portions of the detection circuitry in order to discern drop fall (6).

PERFORMANCE SUMMARY

The features of the detector include the temporary disconnection of the self-contained oscillator from the potentiostat by means of an analog switch as soon as drop fall has been detected which eliminates the need for filtering. A single adjustment generally suffices for a wide range of potentials, and the operation of the detector is unaffected by the presence of the pzc within that range. The response time, between 100 and 200 μs, is dictated by electrochemical cell characteristics, the frequency of the ac perturbation, and the time window of the missing-pulse detector. Unfavorable cell conditions are those in which large faradaic and nonfaradaic components are present so that the output of the tuned amplifier remains substantial even after the drop has fallen. Such circumstances are encountered, for example, with a solution of 1 mM Cr^{3+} in 1 M $NaClO_4$ (pH 3) at an electrode potential of -1100 mV. vs. SCE where the diffusion-controlled reduction of Cr^{3+} occurs, and the excess electrode charge density is large and negative (ca. -13 μC cm^{-2}) (13). The response time was assessed by observing the current-to-voltage converter output on a Biomation Model 820 transient recorder in the pretrigger mode. Detection was considered to have occurred when sinusoidal variations at 100 kHz could no longer be distinguished in the cell current. Thirty determinations yielded an average detection time of 185 μs with a standard deviation of 36 μs. Measurements at the growing mercury drop are essentially unaffected by the ac perturbation since it is automatically disconnected within this time scale. Either individual or successive natural drop times can be conveniently determined to this accuracy, so that current–time curves may be monitored even at subsecond sampling times with high accuracy. In addition to its use as a synchronization device for rapid dc polarography (see ref. 4 for details) and determinations of the excess electrode-charge density from charge–time curves (14), we have also found it to be highly suitable for obtaining precise surface-tension data from drop-time measurements (11).

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Apparatus for the Dynamic Coating of Capillary Columns

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The use of glass capillary columns is expanding rapidly in the analysis of the complex substances by gas chromatography. The glass column is still costly and it is sometimes convenient for the user to control length, nature of liquid phase, and thickness of stationary phase of the columns to be used.

Recently several workers (1–3) have reviewed the numerous recipes available for the preparation of columns. Thus many of the myths have disappeared. The manufacture of a column requires the careful attention of the pretreatment of the glass surface, the deactivation of its Lewis acidity, and finally the coating of the stationary phase. One of the most reproducible methods of coating the column is a variation of the dynamic method developed by Schomburg and which has been called the mercury plug technique (4). The method consists of introducing a short mercury plug immediately after the liquid phase has entered the column. This technique aims at achieving a thin film from a highly viscous solution which can resist drainage and non-uniformity of the coating during the evaporation stage. This method is relatively fast and has the potential that the same equipment can be used for other steps such as coating with a deactivating agent or rinsing the column.

A simple apparatus has been developed which is designed to coat the columns and is capable of introducing a short plug