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Authors

Goldsworthy, William W.
Clem, Ray G.

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A DIGITAL POTENTIOSTAT*

William W. Goldsworthy and Ray G. Clem

Nuclear Chemistry Division and
Lawrence Radiation Laboratory
University of California
Berkeley, California 94720

May 1971

Sir: Reported, for the first time, is an instrument for potentiostatic control of an electrochemical cell employing a new technique--digital current feedback. Digital current pulses, which can be scaled to read-out directly on a scalar the weight of sample oxidized or reduced, pass through the auxiliary electrode of the cell and are used to maintain a control-potential. The potential-control rise-time of this device is limited primarily by the RC characteristics of the cell and, to a minor extent, by the size of the digital current driver and the dead time between pulses. This development entirely obviates the need for elaborate phase correcting networks presently required to prevent potentiostatic overshoot or oscillation. In addition, current-time information appears at the output of the device in the form of a pulse train and is thus directly computer compatible. The use of a current to voltage converter and a voltage to frequency converter required for computer compatibility with conventional analog systems is eliminated. Since the instrument operates simultaneously as a potentiostat, a current to frequency converter, and subsequently as a digital integrator, a new term--digipotentiogrator and abbreviated DPI has been coined to identify it. The title of this article may, however, find more general acceptance. The further advantages of this new design are improved sensitivity and stability, design simplicity and a large reduction in costs for components and assembly. Extensive use of integrated circuits is made. Also its size and weight is small and the power requirements are quite low.

The arrangement shown in Figure 1 is used to digitally maintain a control-potential and to digitally measure the charge transfer which occurs in an electrochemical reaction. Two charge sources are connected to the auxiliary electrode. One source injects charge digitally, while the other source, which is a constant current driver, extracts charge on a continuous basis. Both drivers are designed to deliver up to 1-mA of average current and to perform independently of the potential of the auxiliary electrode.

The cell's reference electrode is connected to the positive terminal of a differential comparator through a unity gain impedance coupling amplifier and the desired control-potential is applied to the negative terminal. Any positive output from the differential comparator-balance detector initiates operation of the digital charge pump for fixed time periods and at rates determined by the charge demands of the cell. A local 500 kHz crystal clock furnishes digital injector drive intervals up to the clock frequency and therefore provides very good digital resolution. Since the charge demand sampling is made only during the times between possible injector drive intervals, the occurrence of a partial current drive interval is prevented.

The small value capacitor C_1 is attached from the reference electrode to the grounded working electrode to maintain potential-control when the cell is driven through its electrocapillary maximum potential.

Figure 2 illustrates the current and voltage response in time to a -500 mV to ground square-wave applied to the control input of the DPI when employing a capacitive-resistive simulated cell load. The digital current feedback pulses, which are initially applied at the clock frequency and thus appear as a blur on the time base selected, drive the control potential from

-500 mV to ground. Once ground is reached, only occasional pulses are required to maintain the control-potential. These pulses have an average frequency of about 4 kHz and a displacement in the control-potential of approximately 10 mV. Note that, in this system, the descent time is limited only by the current capability of the digital charge source and by the dead time between pulses. The use of a 10 mA charge source would, for example, reduce the descent time by a factor of 10.

Figure 3 shows a repeat of the above experiment but now using a modified Matson et al cell (3) and employing 0.01M KCl as the supporting electrolyte. The potential excursion is less than that shown in Figure 2 because the square-wave is now applied against a SCE. Although the descent time is somewhat longer owing to the solution resistance and the dynamically changing cell capacitance, it is adequately fast for our present purposes. A pulsed current extraction rate of roughly 8 kHz is required to satisfy the background current demand at a control-potential of 0.0 V vs. SCE. This frequency is greater than the electron-transfer rate of electroactive substances and is therefore of no consequence.

The current drift of this device amounts to only 0.04% over a period of 1.4 hours. The study was made by imposing a control-potential of -1.000 V against the simulated cell. The average count rate was 24,000 for a 10-sec current sampling interval. The internal potential control of the DPI is better than 1-mV.

Figure 4 is an anodic-stripping voltammogram taken with the DPI employing the required peripheral gear described in a previous paper (1) and using the cell mentioned earlier (3).

The presented instrument is a unipolar device because it was developed solely for anodic-stripping analysis in conjunction with an ongoing environmental study. A more sophisticated bipolar instrument is presently under development and will be reported in the near future. One should note that direct grounding of the cell's working electrode eliminates bothersome induced currents present in the floating working electrode designs. Location of the drop separation time when applying the future instrument to polarography will be simplified. A drop separation signal can easily be derived by sensing the abrupt current-pulse spacing changes which occur at the end of the life of a drop.

In conclusion, this approach to direct conversion of charge to a digital number appears to be quite generally applicable. The same principles which resulted in the development of the digital integrator (2) and the digital nuclear spectrometer (3) has now been applied to electrochemistry. If the pulsed current source in the present application were replaced with a broad spectrum pulsed light source and the electrochemical cell replaced with a phototube, direct digital conversion of spectrophotometric data for an absorber in the pulsed light path would result.

(ACKNOWLEDGEMENT

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LITERATURE CITED

* Work performed under the auspices of the U. S. Atomic Energy Commission.

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- (2) R. G. Clem and W. W. Goldsworthy, *ibid.*, 43, 918 (1971).
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FIGURE CAPTIONS

Fig. 1. Digipotentiogator, (DPI) Block Diagram.

Fig. 2. DPI transient response for a dummy cell.

upper trace: Current pulses

lower trace: Control-potential response

time base: 250 μ sec/division

Fig. 3. DPI transient response for an electrochemical cell (1). Parameters

the same as for fig. 2.

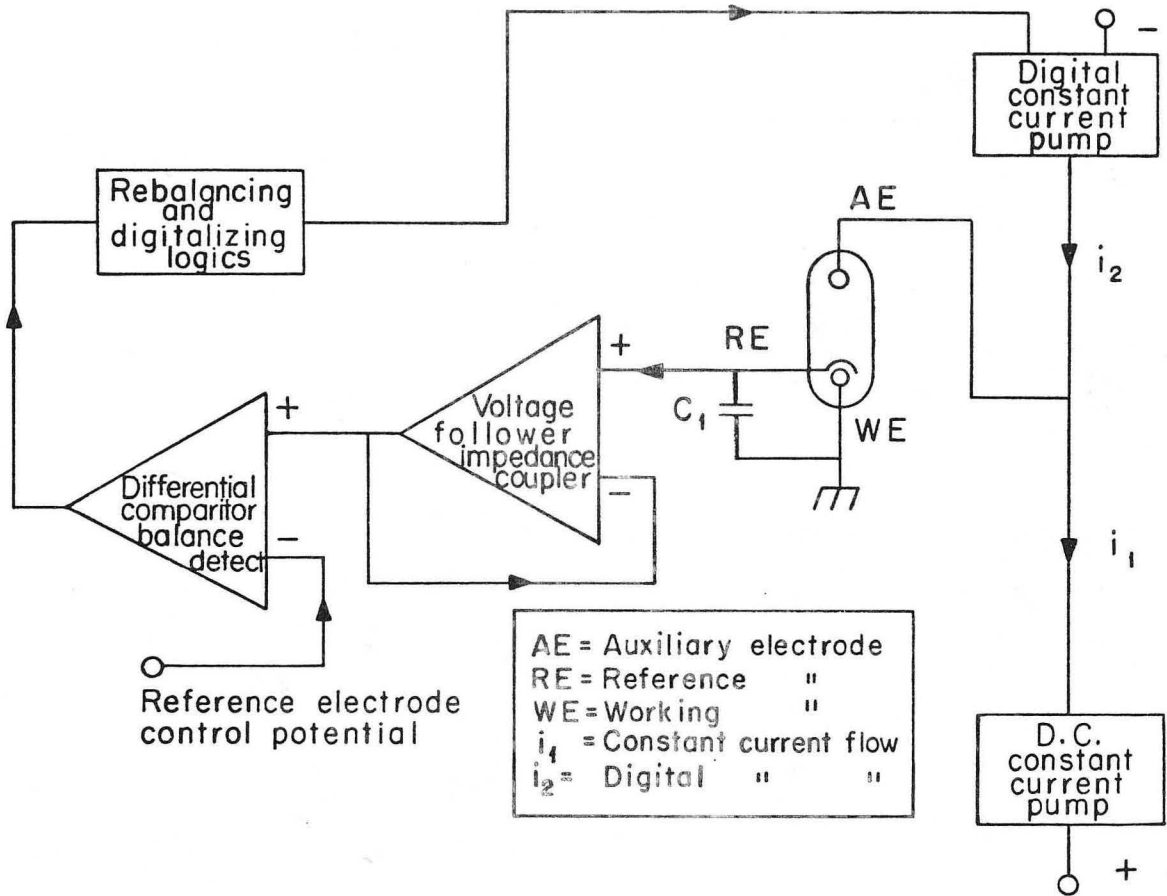
Fig. 4. Anodic-Stripping Voltammogram

Solution: 0.01M KCl, 67 ppb. Pb^{2+} .

Conditions: -1.000 V vs. SCE starting potential. Incremental ramp step

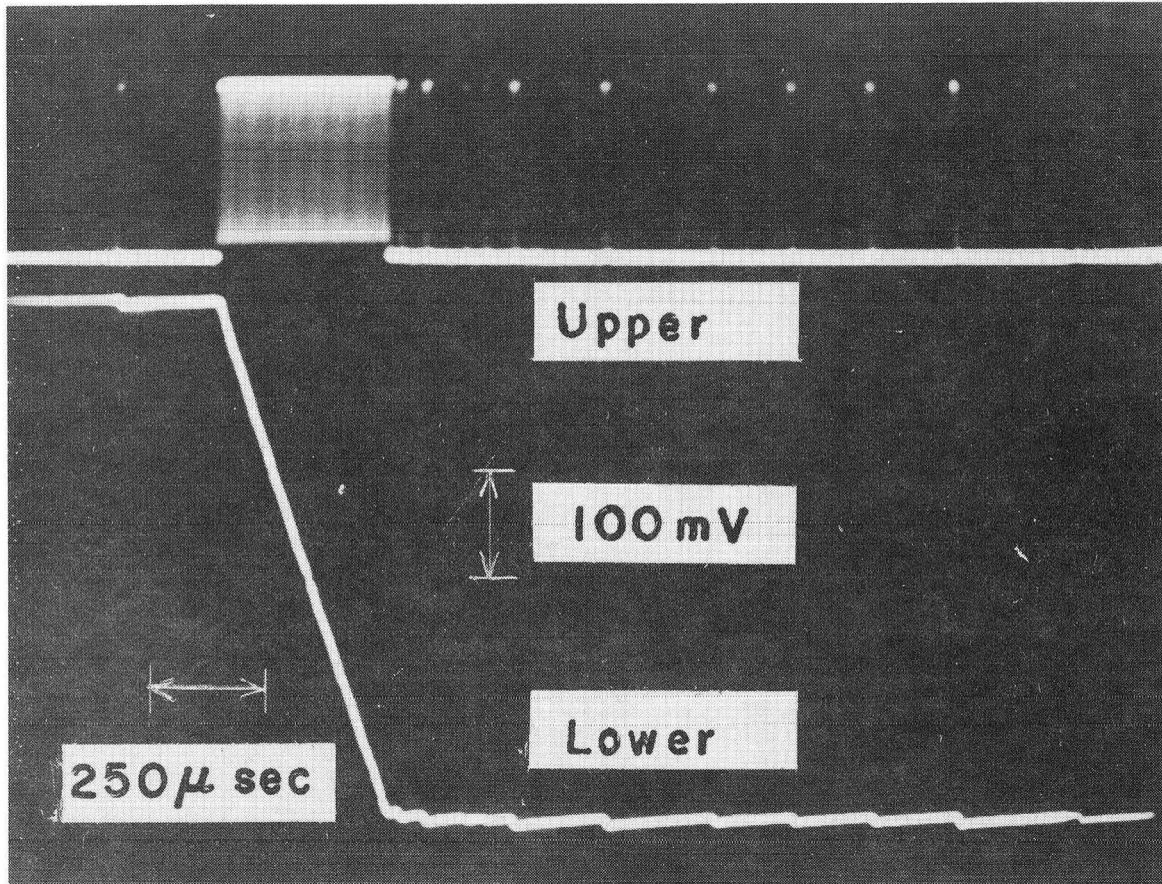
\approx 5 mV, ungated analyzer input employed. Dwell time =

1 sec/channel.



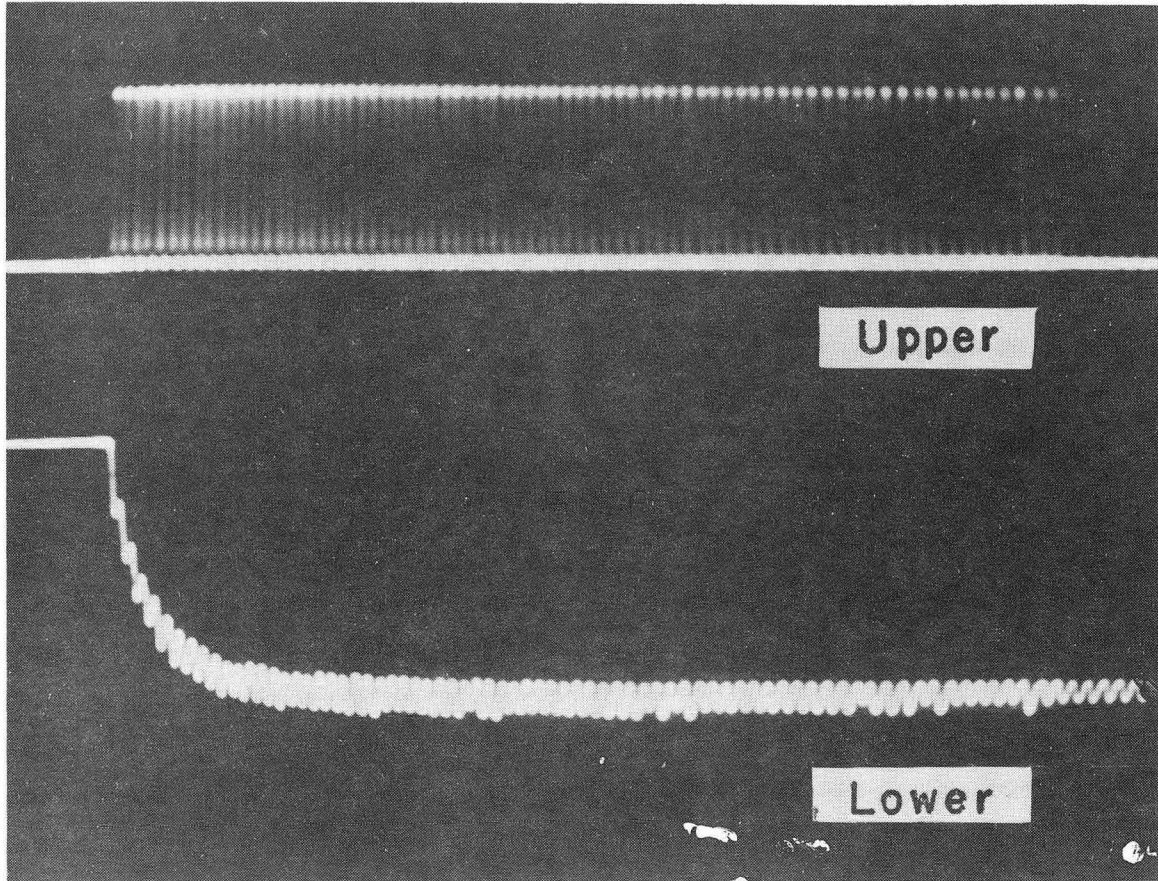
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Fig. 1



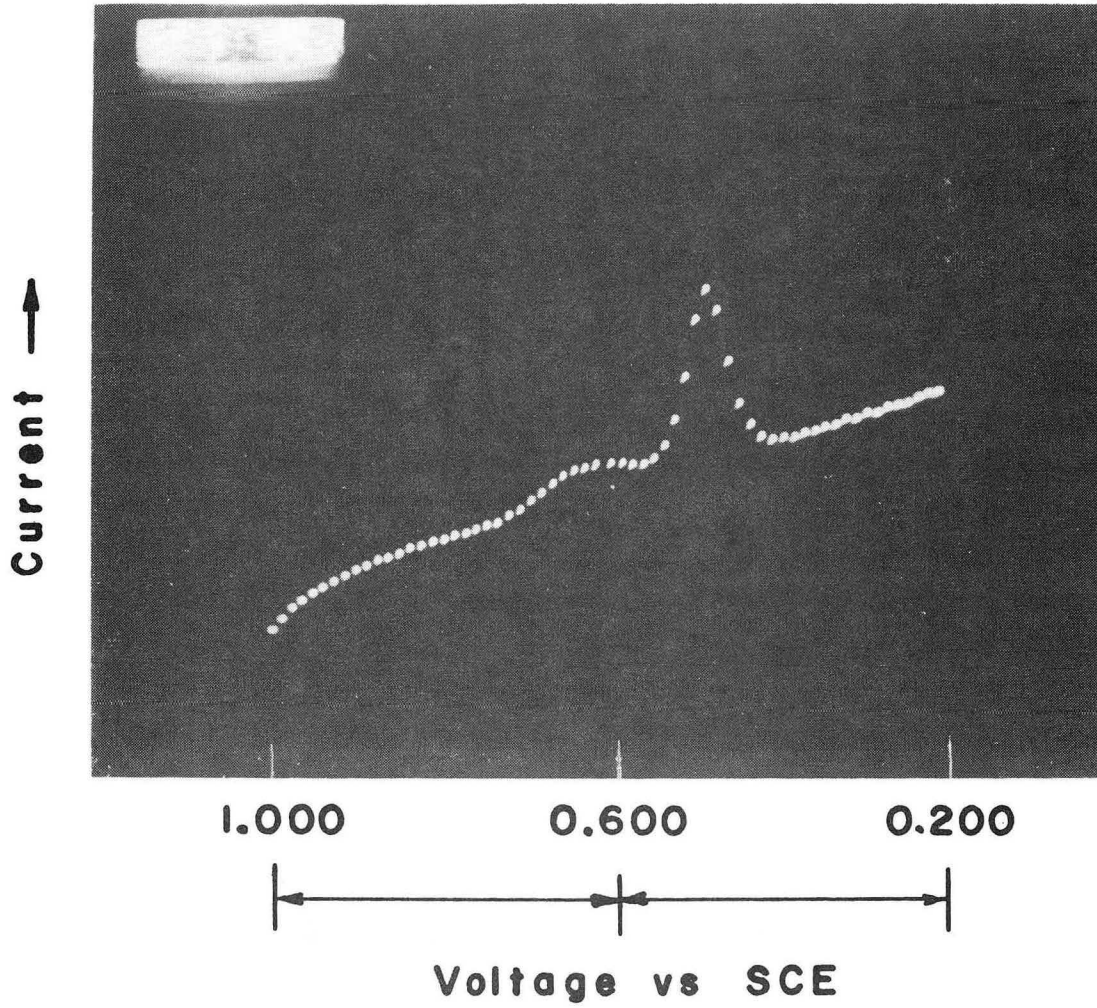
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Fig. 2



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Fig. 3



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Fig. 4

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