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A MODULARIZED DIGITIZING TIME-SYNCHRONIZING
CURRENT-SAMPLING SYSTEM FOR
ELECTROANALYTICAL STUDIES*

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BRIEF

A digital recording system consisting of several function modules and
having a measuring precision of 0.02% full scale is described and its use in
coulometric and in modern polarographic applications is discussed.

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ABSTRACT

This instrument consists of a collection of function modules which, when appropriately interconnected, can be used to synthesize most of the instruments useful for electrochemical analysis. All data are recorded in digital form and are stored in a pulse-height analyzer operated in the MCS-mode. The measuring equipment is capable of a precision of 0.02%.

The application of this system to controlled-potential coulometry without and with normalization of the background current and to predictive coulometry by data processing of the stored information is described. Also, the use of the instrument for conventional, subtractive, differential, and incremental derivative polarography is discussed.
Analog readout devices, such as meters and servo-recorders, are not capable of the measuring precision available from the output of electrochemical instruments constructed from high quality operational amplifiers. These readout devices are limited as to response time, accuracy, and resolution. Also, the data obtained are in their final forms, and further automatic data processing is not performed readily. Fortunately, digital data accumulation and processing permit a high rate of data collection and greater accuracy, resolution, and precision; the digital data are eminently suitable for further data processing by a computer, thereby expanding the scope and allowable complexity of the experiments undertaken. Several workers before us have used digital recording in electrochemical studies to their advantage (1-6).

The digitizing, time-synchronizing current-sampling system presented here consists of a collection of function modules which, when properly interconnected by means of a patch panel, can be used to synthesize most of the instruments useful for electrochemical analysis. Some of the modules employed were designed specifically for this project, whereas others were adapted from published circuits, purchased commercially, or were obtained through this laboratory's production shop facilities as LRL designed instruments. Although a pulse-height analyzer (PHA), operated in the multichannel scaling mode (MCS), is used to record and store digital information, this paper should be of general interest to those workers possessing a small computer, for it is quite likely that the timing, synchronizing, and digital recording functions described herein could be duplicated by the use of software.
For the purposes of this report, the system is presented as being electrochemically dedicated; however, it is obvious that with the proper interfacing it could be used to control a spectrometer or other device and to store the resulting digital information. The additional uses of a PHA in radio-chemical and X-ray fluorescence applications are well known. Justification for such an analytical data acquisition system lies in the fact that the analytical work performed here is non-routine. The size of the samples submitted is often limited owing to their nature or expense and, quite often, the precision required cannot easily be attained with wet or analog instrumental techniques. This system permits a high degree of flexibility and is capable of a higher measuring precision than that provided by conventional analog instruments.

It is improbable that any one group will want to duplicate this system in its entirety although some features will probably be of interest to many groups.

The studies presented are those which show the versatility of the system. Automation of controlled-potential coulometry by the use of a time programmer or a limit rate meter is discussed. Predictive coulometry is performed by the use of a signal router to distribute data between two scalers operated at preselected time intervals or by the use of a data processor and a pulse-height analyzer, operated in the multi-channel scaling mode, to distribute data as a function of time. Subtractive normalization by data processing of the log \( i \)-time curves of small samples results in virtual elimination of the background current contribution, thus improving the accuracy and sensitivity of the titrations.
A polarographic precision 13 times as great as that obtainable by measuring total drop current is realized, and sensitivity at the $10^{-7}$ M level is obtained by the judicious selection of the current-sampling period and location during the life of a drop. Subtractive polarography becomes a practical reality through a subtractive transfer of data between memory locations, since the same capillary electrode is used to obtain the background-current scan and the sample scan. This technique normalizes the background and thus makes the diffusion-current measurement more precise and increases polarographic sensitivity to the $5 \times 10^{-9}$ M level. One should note the conspicuous absence of drop-frequency filters, drop knockers, and other familiar equipment usually associated with modern polarography.

INSTRUMENTATION

The conversion of the charge involved in electrochemical reactions to digital information is made at an early stage in the system described in order to improve accuracy, sensitivity, and to aid in the convenience of handling data. The early stages of this digital system are quite similar to analog systems used for electrochemical studies. A divergence from conventional charge
sensing integrator design produces, instead of a potential, a train of pulses proportional to the integral of $V_i \, dt$ where $V_i$ is the output potential of the current to voltage converter. These pulses and the drop separation timing of the dropping mercury electrode (DME) are all the information necessary for digital data processing of the currents involved in an electrochemical reaction. The remaining circuitry, with the exception of the ramp generator, is used to process digitally this information by appropriate synchronization, sampling, incremental differentiation, arithmetic, storage, readout and display. A ramp generator furnishes the desired sweep to the potentiostat for polarographic studies.

In Figure 1 a block diagram illustrates the digital electrochemical system used for coulometric and polarographic studies. The basic components of this system needed for coulometric analyses are denoted with solid lines. Those shown with dotted lines are used additionally for polarographic analysis. The basic components pertaining to coulometry are the potentiostat, the current to voltage converter, the digital integrator, the scalers, the pulse height analyzer, the signal router, the limit rate meter and the timers. Additional components, required for polarography, are the multifunctional voltage ramp generator, the drop separation sensor, the polarographic timer, the digital differentiator and the signal sampling gate.

Potentiostat. The potentiostat shown in the block diagram of Figure 2 is quite conventional (7). It is designed for output currents of 100 mA at voltages of ±100 V and allows for local or remote control of the reference electrode potential.
The circuit uses a Zeltex 140B control amplifier with approximately $10^7$ open loop gain, followed by a high output current complimentary emitter-follower to drive the electrochemical cell.

A high impedance differential input amplifier arrangement, consisting of three Philbrick P2AU operational amplifiers, senses the reference electrode potential and compensates for potential offset introduced by changes in impedance at the input of the current to voltage converter. Impedance charges result from current scale range changes.

The reference electrode potential can be controlled locally by a potentiometer, remotely by the multifunctional voltage ramp generator or as a function of the output of the current to voltage converter to obtain constant current operation from the potentiostat.

**Current to Voltage Converter.** The current to voltage converter and inverter, which consists of two Zeltex M141 operational amplifiers, converts cell current to a proportional voltage, provides a selection of current ranges and output polarity control and delivers current feedback for external control of the potentiostat when constant current operation is desired. Its bipolar output is used to drive the unipolar input digital integrator which follows it.

**Digital Integrator.** The digital integrator shown in Figure 3 integrates the output potential of the current to voltage converter and converts it to a train of pulses whose number is proportional to the integral of $V_1 \, dt$ plus that charge delivered by the offset current control $R_3$.

The advantages gained by converting to digital form are: the virtual elimination of the hysteresis error associated with charging and discharging
of the charge storage capacitor of the conventional active analog integrator by allowing only small potential variations to occur across it; greatly improved linearity, since the active integrator is used solely as a null amplifying device; and extremely good reading definition due to the high digitizing rate available.

The integrator functions in the following manner. Current flowing through resistor $R_1$, as a result of an input potential being impressed, causes the active integrator to start charging capacitor $C_1$. This produces a demand for rebalance through the active integrator output unbalance which is sensed by a differential comparator and then causes the opening of the clock pulse gate. Locally developed clock pulses flow through this gate, through a differentiating network, and into the input of a timing "one shot." With each passing pulse the "one shot" is triggered. Its timed output drives the charge extractor and the output driver. Signals from the output driver are used later for data processing. Each time the charge extractor is driven, a metered amount of charge is extracted from the input of the integrator. The quantity of this charge is directly proportional to the current flowing through the extractor and to the time duration of extractor operation. The current flowing through the extractor is also equal to total input current, since a continuous input balance is maintained. By controlling the output period of the timing "one shot" the duration of the extractor intervals can be adjusted so that each represents the extraction of a discrete amount of charge, or equivalent weight of oxidation or reduction.

Potentiometer $R_3$ supplies a source of plus or minus integrator input offsetting current to allow offset operation when input potentials may cross
the zero intercept during polarographic scanning. The capacitor $C_2$ furnishes a temporary sump for input charge, giving the operational amplifier of the active integrator more time to pump charge into capacitor $C_1$. This is quite important in cases in which the operational amplifier used cannot supply output current fast enough to follow the rapid initiation of current extraction. The inexpensive Fairchild 702 integrated circuit operational amplifier used allowed exceptional linearity to be obtained over a four decade range. This linearity was 0.02% at full scale. Integrator stability held to 0.02% for days. To aid in system data processing, a sampling gate is also incorporated, permitting output data flow at the command of the polarographic programmer.

**Limit Rate Meter.** This instrument shown in the block diagram of Figure 4 consists of a count-rate meter followed by a potential comparitor, a block flip-flop and an output driver. It will terminate a coulometric titration only on a descending count rate (8). To initiate operation, the flip-flop is reset, allowing the output driver to ungate the accumulate scaler which sums the output pulses from the digital integrator. When the pulse rate falls below a pre-selected level, operation of the accumulate scaler is inhibited, thus terminating the measurement. A hysterisis generator is employed in conjunction with the comparitor only to insure against accidental shut-down during the onset of a measurement.

**Multifunctional Voltage Ramp Generator.** Figure 5 shows the essential features of the multifunctional voltage ramp generator used in making polarographic scans. This device employs integrated-circuit logics to determine ramp sense and limits, and to provide means for resetting, starting, stopping, stepping, and holding the ramp. Five kinds of ramps are available: single, multiple, bidirectional, step-and-hold, and stair-step.
Conventional voltage-ramp generation occurs when current is allowed to flow into the input of its active integrator. Control of rise or fall times range from 1.5 to 1000 sec, and adjustable potential ranges of 1, 2, 3, and 4 volts are provided with means for absolute calibration. The ramp can be started, stopped, or restarted anywhere within its cycle. Stair-step voltage-ramp operation results when the current flowing into the input of the active integrator is on command of an externally triggered one-shot timer. Stair-steps of 1 to 15 mV are readily obtainable with rise times on the order of milliseconds and dwell periods adjustable to several seconds.

**Drop Separation Sensor.** Synchronization of digital data acquisition with the DME drop time, when making polarographic studies, is extremely important if statistically generated errors are to be avoided. The drop separation sensor of Figure 6 senses the change in cell impedance at the instant of drop separation in the DME and delivers an output synchronizing pulse each time drop separation occurs (9,10). A 250 KHz signal is used as a source of sensing signals. Its high frequency and low level minimize interference with measurements. The 250 KHz signal is divided between the cell and the 100 pF capacitor $C_1$. As drop separation occurs, the impedance and thus the ac potential across the cell rises. This rise is amplified, detected and used to drive a Schmitt trigger circuit which supplies the synchronizing pulse for the polarographic programmer. Resistor $R_1$ must exhibit a sufficiently high impedance so as not to shunt too much of the 250 KHz signal going from the cell to the amplifier.

**Polarographic Programmer.** The polarographic programmer shown in Figure 7 supplies the sampling time delay from the inception of each drop and the control of timing for each data sampling interval necessary for performing accurate polarographic analysis.
It consists of two sequentially timed "one shot" timers. The first times the delay period and the second the signal sampling period. Both have timing ranges of from 1 msec to 1.8 sec. Reproducibility for a 1-sec sampling period is better than 0.01%.

**Incremental Digital Differentiator.** The instrument shown in the block diagram of Figure 8 can be used with a DME or a solid electrode (9) to obtain incremental derivative polarograms. The data acquisition process with a DME is synchronized by sensing drop detachment. With a solid electrode an auxiliary timer supplies synchronizing impulses for data acquisition. Figure 9 shows how incremental digital differentiation is simulated. As pulses from the digital differentiator, representing charge transfer in the electrochemical cell, occur during the first sampling interval, the number of these is stored in the first memory channel of the analyzer. The control-potential is then stepped to its next value, and the analyzer is instructed to store additively the number of pulses obtained from the next sampling interval. Thus, a number equal to the difference in the numbers obtained in the first and second current sampling intervals remains in the first memory channel of the analyzer. At the inception of the next sampling interval, advancement of data acquisition is made to the next memory channel and the process is repeated until the scan is completed. This approach is similar to differential polarography, except that the difference scan is made on a point by point, rather than on a scan by scan, basis.

The incremental differentiator operates in the following manner: delay period pulses originating in the polarographic programmer simultaneously toggle the steering "flip flop" and trigger its wait-gate generator. The steering flip-flop
delivers add-subtract logic commands, as a function of its state. The wait
gate generator along with "AND" gate 2 allows a channel advance command to be
developed each time the gate output is true. This occurs only when the
steering flip-flop is in its Q state. A ramp advance command is developed
each time the "AND" gate 1 output is true. This occurs only when the steering
flip-flop is in its Q̅ state and a delay period input is present. The delay
produced in the wait-gate generator avoids interference between add-subtract
steering and the analyzer's channel-advance cycle by time shifting the channel
advance command from those of add or subtract. RC slow down filters, inserted
in series with the analyzer's add-subtract inputs, prevent interference with
information, held in the analyzer's memory accumulator during the add-subtract
switching cycle.

Multichannel Pulse-Height Analyzer and Data Processor. A Northern
Scientific Model 610 1024-channel pulse-height analyzer, operated in the multi-
channel scaling mode, is used for polarographic and coulometric studies and
permits potential-related storage in the analyzer's memory as a function of
channel, thereby providing the high information storage rate needed for pre-
cision measurement. Some minor modifications of the analyzer had to be made
to expose the necessary logic command functions of add, subtract, channel
advance, readout, accumulate, stop, start, and reset needed for control.

The Northern Scientific Model 400 Data Processor permits limited
arithmetic manipulation of stored data between the first and second halves of
the analyzer's memory. For example, it is possible to transfer data from the
first half of the memory to the last half and simultaneously multiply it by
powers of ten; normalize data in the last half of the memory by powers of ten;
and sum data within selected channel regions in the first half of the memory, and record the resulting summation in the second channel of the last half of the memory. This instrument can also convert stored information to a five-cycle logarithmic signal, which can be either displayed on the analyzer's scope or read out on an X-Y plotter.

**Miscellaneous.** In addition to the foregoing modules, several other function units are needed to complete the system. These are program timers, scalers, a signal router, a plotter, a printer, a potential source, a digital voltmeter, and a dual-trace oscilloscope.

The two high-precision digital program timers LRL 15 x 841 used are capable of operating at selectable, single or periodic, timing intervals, ranging from 0.01 msec to 1000 sec. One of these timers is used to control the duration of the coulometric or polarographic measurements. The other supplies simulated drop-separation timing for sample-period advancing when a solid or a mercury-pool electrode is used. It also serves as a signal routing controller during coulometric titrations.

Two $10^6$-capacity scalers, LRL 15 x 911A function as accumulators. Generally, one of these is used; however, it is possible to divide data between the two scalers for selected time periods by the aid of the auxiliary timer and the signal router LRL 15 x 994 during predictive coulometry.

A Mosely, Model 2D-2, X-Y point plotter, equipped with a null detector, is employed to plot out stored digital information from the analyzer. Stored numerical information can also be printed out on paper tape at the rate of 40 lines/sec, by use of a Franklin, Model C-1220D-10-6L12-R, printer.
A Fairchild, Model 7050, digital voltmeter allows continuous visual display of the cell reference-electrode potentials or of the current to voltage converter output potentials, and is helpful in locating end-point potentials in constant-current coulometry.

A power Designs, Model 2005, high-precision potential source, in conjunction with precision resistors, permits calibration of the current to voltage converter, the integrator, and the digital voltmeter.

A Hewlett-Packard Model 132A, Dual-Beam oscilloscope aids in visually examining wait-gate alignment of the polarographic programmer with respect to drop time.
EXPERIMENTAL PROCEDURE

Reagents. Supporting electrolytes and standard metal-ion solutions were prepared by dissolving weighed quantities of reagent-grade materials and then diluting to volume in distilled water. The nitrogen used was of high purity. The mercury used was of instrument grade and was obtained from Masero Laboratories.

Apparatus and Procedures. The coulometry cell used was similar to the one described by Harrar (11), and a conventional DME assembly was employed in conjunction with a ≈ 1-sec Smoler capillary electrode for polarographic studies. Prior to voltage scanning or titrating, all solutions in which oxygen was an interference were purged with nitrogen for at least 10 min. Exclusion of oxygen was assured by maintaining a flow of nitrogen over the solution during the electrochemical operation.

RESULTS AND DISCUSSION

Constant-Potential Coulometry. Controlled-potential coulometric titrations can be performed by our system at several levels of automation. In its simplest form, involving total titration of the sample, only the basic modules—the potentiostat, the current amplifier, the digital current integrator, and a digital accumulate scaler for readout of the coulombs consumed—are used. The titration is stopped manually by the operator when the cell current, displayed on a panel meter, falls to a predetermined level. Considerable operator attention is required. Addition of one of the time-programming modules, capable of turning the instrument off after a fixed time interval, adds some automation to the system and frees the operator, but does not make best use of his time.
The minimum time interval chosen is necessarily that time interval required to
titrated the largest sample. Inclusion of the limit rate meter module automatically terminates the titration when the output of the digital integrator falls below a preselected pulse rate. This module, then, provides on a digital basis the same function as that described on an analog basis by earlier workers (8). The time required for titration is tied to the sample size and the operator is freed in the interim.

**Predictive Constant-Potential Coulometry.** To decrease the time necessary to obtain a result, several predictive coulometric methods have been offered involving only partial titration of the sample, the end point being determined either by extrapolation or by calculation (6, 12-15). These methods are based on the assumption that the electrolysis current follows Lingane's equation (16),

\[ i = i_0 e^{-kt} \]  

(1)

where \( i \) is the current at time \( t \), \( i_0 \) is the initial current, and \( k \) is the electrolysis rate constant. If the system under study conforms to this equation, one may calculate the number of coulombs consumed at the titration end point, using an equation derived by Meites (15).

\[ Q_\infty = \frac{Q_2^2 - Q_1 Q_3}{2Q_2 - (Q_1 + Q_3)} \]  

(2)

\( Q_1, Q_2, \) and \( Q_3 \) are the coulombs consumed at times \( t_1, t_2, \) and \( t_3 \), respectively. The equation is derived by setting \( (t_2 - t_1) = (t_3 - t_2) \). One may employ this predictive equation, using our system, in two ways. Two time-programming modules and a signal router are required in addition to the basic modules above.
One time programmer is set to run continuously and serves only to turn on all required equipment simultaneously. The other provides equal preselected time pulses to operate the signal router, which distributes the digital integrator's output pulses between two gated accumulate scalers. Sufficient data are accumulated to permit calculation of the titration end point, using a small desk computer, in considerably less time than that necessary for complete electro-reduction or oxidation. The second approach again uses the two time programmers, but now employs a pulse-height analyzer, operated in the multichannel scaling mode, to store the output from the digital integrator. The second time programmer is used to serially advance the analyzer's memory channels at equal preselected time intervals. The stored data can be displayed linearly or, by use of the data processor, logarithmically on the analyzer's display oscilloscope. This logarithmic display is very useful in evaluating an existing method or in developing a new method, for it allows one to determine the linear region of the current-decay curve. Integration of selected channels in the linear region, using the data processor, permits the expansion of the time interval and thus decreases the error in calculating the titration end point (6). When samples are titrated that are so small that the background current is an appreciable fraction of the total cell current, some improvement in the accuracy of the titration is realized by subtractive normalization of the stored information, again using the data processor. Figure 10, curves A and B, shows the results of a lead titration without and with normalization, respectively. Although a titration error of only 2 μg is found, two problems are attendant. This method is subjective, and the 5% nonlinearity of the logarithmic display system, although adequate for normalizing data from titrations of larger samples, becomes
increasingly less so as the titration current approaches the background current. These difficulties are eliminated by the use of an iterative computer program to linearize the data. This program will be reported on in the near future.

This second approach encourages the development of coulometric methods for systems that would be very difficult or impossible to deal with by the conventional analog technique. For example, it was shown that Pd(II) could be determined titrimetrically by oxidation to the four-valent state with hypochlorite (17). Recently it was found that Pd(II) can also be electro-oxidized to the four-valent state in the presence of azide at 0.850 V vs SCE, but with low current efficiency. Electroreduction of Pd(IV), however, proceeds with 100% overall efficiency within a reasonable time at +0.100 V vs SCE. A 75-μA termination point is used. If present, Pt(IV) is co-reduced at this potential, since +0.100 V is on the foot of its reduction wave, resulting in a higher final current than the termination current used in the absence of Pt(IV). Furthermore, the final current varies with the Pt(IV) concentration. This behavior would generally prevent development of a palladium method on the presence of Pt(IV), even though platinum does not interfere in the reduction itself; in fact, its presence reduces the time necessary for the Pd(IV) reduction by the following cyclic reaction:

\[ \text{Pt(IV)} + 2e^- \rightarrow \text{Pt(II)}, \]

\[ \text{Pd(IV)} + \text{Pt(II)} \rightarrow \text{Pd(II)} + \text{Pt(IV)} \]

Using the log current-time display, it is possible to determine palladium by locating the channel at the extrapolated intersection of the descending and horizontal branches of the current-decay curve, and by using the data processor
to integrate all preceding channels to this point (see Figure 11). Acceptably small positive errors of a few tenths of 1% are obtained in the presence of more than 50 times as much Pt(IV) (by weight) as palladium by this approach. This procedure will be reported in full later.

Constant-Current Coulometry. By turning a selector switch, the potentiostat is converted to an amperostat. One-time programmer is used to turn the instrument on and off and also provides selected electrogeneration times ranging from continuous operation to 10-μsec intervals. This feature is very helpful in locating constant-current coulometric titration end points by potentiometry.

DME Polarography. A review of the more successful attempts and the development of the necessary methodologies to improve the sensitivity of conventional polarography is given by Meites (18). Our system makes use of these developments but there is no need for the familiar devices associated with analog signal recording. These differences as well as other advantages will become obvious in the following exposition.

Figure 1 indicates the modules required for polarography and Figure 9, lines A through F, shows the time sequence of operation. The stairstep voltage ramp shown in Figure 9E is employed throughout the polarographic studies below since its use eliminates the potential charging of the electrode double layer during the current-sampling interval.

Table I shows the effect the sample gate width has on the precision of current measurement on a solution of cadmium. In view of these data, a gate interval wider than 30 msec should always be used since shorter sampling times result in a decrease of precision owing to a decrease in the signal averaging.
of short-term current fluctuations. The fact that the smallest error is found at 50, 200, and 300 msec indicates some 60 Hz line frequency pickup even though shielding and grounding precautions were observed. It is interesting to note that the relative average deviation of the gated drop data, at times greater than 30 msec, is less by a factor of 13 than that for the ungated drop.

Table II summarizes the effect the sample gate position has, at constant width, on the signal-to-background ratio (S/Bkg) for cadmium. These data permit balancing the increasing count accumulation at increasing gate widths with the continual decrease in the S/Bkg ratio, and thus to select an optimum gate width and location under open circuit conditions. For a 1-sec drop a 450 to 500 msec wait interval followed by a 400 msec gate interval allows the accumulation of about 40% of the total counts for the ungated drop, with a sensitivity decrease of only 10%. A high count accumulation is advantageous for subtractive polarography discussed below.

The detection limit of this method for well-behaved electroactive species, such as lead and cadmium is about $10^{-7}$ M. The arrow in Figure 12 points to a lead contamination wave just discernable form the background current. Anodic stripping analysis fixed the lead concentration at $1.1 \times 10^{-7}$ M.

The last three columns of Table III are data stored on three consecutive scans on the diffusion plateau of the cadmium wave. The same starting potential is used for each scan and increases in going from the bottom to the top of each column. Although small variations are evident on a scan to scan basis, the total number of counts in each column agree with the average of the three within a few hundredths of a percent.

Incidental to these studies, it was observed that polarograms obtained by current-sampling at the inception of the drop are insensitive to moderate stirring. This should promote the use of the DME in amperometric titration, even though some sensitivity is lost and the precision reduced. See Table II.
Subtractive Polarography. In principle, one of the most promising approaches to high-sensitivity polarography is subtractive polarography (19); however, many experimental and instrumental difficulties arise when one applies conventional analog techniques to this approach. These experimental difficulties occur because of the very small probability of obtaining two identical capillaries. The use of two similar capillaries, in conjunction with dual systems of drop-time controllers, signal filters, and a balance amplifier in one channel, permits the performance of subtractive polarography but not with the sensitivity one might hope to achieve. The variations in the mercury flow rate and drop time characteristics of the similar capillaries over a range of potentials yield a non-linear base line (20).

Our system circumvents all these problems very simply by its ability to record polarographic signals digitally, using the same capillary electrode. To perform subtractive polarography, a solution of the supporting electrolyte is scanned and the digital information is stored in one memory quadrant of the analyzer. A second scan of a solution, containing the supporting electrolyte plus sample, is stored in another memory quadrant. A difference polarogram of the two scans results when the data processor is used to effect subtractive transfer of the first scan into the second scan. The same starting potential, gate setting, and voltage step are used for both scans (see Figure 12). Traces A, B, and C show the results of these operations for cadmium at the $1.12 \times 10^{-6}$ M level. Traces A and B were deliberately offset to aid in their display.

Subtractive polarography offers three distinct advantages to the analyst over other conventional high-sensitivity approaches: polarographic
waves produced by trace-metal impurities in the supporting electrolyte are cancelled; the base line of the sample polarogram is normalized, improving the measurement of diffusion current heights; and (of lesser importance) the sensitivity is increased by roughly a factor of 20 over that stated above.

Consider Figure 13 which shows a difference polarogram of cadmium in a 0.1 M KCl supporting electrolyte taken at the $9 \times 10^{-9}$ M level. Although the points are scattered, the presence of cadmium is indicated. This scattering could be reduced by subjecting the data to a computer curve smoothing operation or by storing repetitive scans of the background and sample solutions prior to the subtractive data transfer.

Although subtractive polarography has a high, real sensitivity, the bulk of polarographic analyses will probably continue to be made at concentrations greater than $10^{-7}$ M owing to adsorption effects at the lower levels. Calibration curves for lead, however, in the range from $10^{-7}$ to $10^{-6}$ M have been prepared which have a precision of better than 5%.

A variation of difference polarography deserves brief mention. If the sample solution is potential-scanned and the information stored in one memory quadrant and if, with the use of a more negative starting potential, a second scan of the same solution is stored in another memory quadrant, subtractive transfer of the first scan into the second scan yields a peak-shaped differential polarogram.

**Incremental Derivative Polarography.** Without the use of an active on-line differentiator, direct digital recording can only approach the true derivative of a signal as a limit. The "incremental approach to derivative polarography" taken by previous workers (9) lends itself to incorporation in
the present system. It differs from differential polarography discussed in the section immediately above in that the incremental derivative is produced on a point by point basis rather than a scan to scan basis. It should be noted that the recorded signal differs only in shape from a true derivative by a constant (9). Despite these shortcomings, this technique serves the same function as the true derivative in restoring the baseline between successive polarographic waves and aids the analyst in detecting electroactive species in the presence of one another which are, potential-wise, poorly separated.

Figure 14 shows the effect of the stair-step potential height on the detection of 1.15 to 1 molar ratios of indium and cadmium whose half-wave potentials are separated by only 50-mV in 0.1 M KCl supporting electrolyte. Although the detection improves as the potential step becomes smaller, even a 10-mV step is sufficient to show that two species are present. Complete resolution of these two elements in this supporting electrolyte is, of course, quite impossible (21).

Table III, the first three columns, are data stored on three consecutive incremental derivative scans of the same solution through the half-wave potential region. The same starting potential was used for each scan, the potential increasing from bottom of the column to the top. The total number of counts agree within a few hundredths of a percent with the average of the three totals, although small variations are evident on a scan to scan basis.

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Table I. Effect of Gate Width on Precision.

<table>
<thead>
<tr>
<th>Gate Width (msec)</th>
<th>counts/drop&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Av. Dev., cts/drop</th>
<th>% Rel. Av. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>565</td>
<td>0.6</td>
<td>0.11</td>
</tr>
<tr>
<td>30</td>
<td>1,828</td>
<td>1.3</td>
<td>0.07</td>
</tr>
<tr>
<td>50</td>
<td>3,150</td>
<td>0.5</td>
<td>0.02</td>
</tr>
<tr>
<td>100</td>
<td>6,153</td>
<td>0.2</td>
<td>0.03</td>
</tr>
<tr>
<td>200</td>
<td>12,377</td>
<td>3.0</td>
<td>0.02</td>
</tr>
<tr>
<td>300</td>
<td>17,659</td>
<td>4.2</td>
<td>0.02</td>
</tr>
<tr>
<td>400</td>
<td>23,189</td>
<td>6.9</td>
<td>0.03</td>
</tr>
<tr>
<td>600</td>
<td>34,560</td>
<td>11.2</td>
<td>0.03</td>
</tr>
<tr>
<td>800</td>
<td>44,350</td>
<td>17.0</td>
<td>0.04</td>
</tr>
<tr>
<td>Ungated</td>
<td>57,836</td>
<td>194.0</td>
<td>0.34</td>
</tr>
</tbody>
</table>

<sup>a</sup>Average of 30 drops.

(4.45 x 10<sup>-4</sup> M Cd<sup>2+</sup> in 0.10 M KCl, E = -750 mV, drop time at -750 mV vs SCE = 1.20 sec, gate closed at 80 msec before drop fall, 9.3139 V = 10,000 cts/sec)
Table II. Effect of Gate Location on Sensitivity.

<table>
<thead>
<tr>
<th>Gate Interval (msec)</th>
<th>cts $^a$</th>
<th>cts $^{b}$</th>
<th>cts Cd $^a$</th>
<th>cts $^{b}$</th>
<th>M x $10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 to 1100</td>
<td>22.0</td>
<td>0.17</td>
<td>5840</td>
<td>1.8</td>
<td>1.67</td>
</tr>
<tr>
<td>900 to 1000</td>
<td>22.4</td>
<td>0.14</td>
<td>5673</td>
<td>3.9</td>
<td>1.75</td>
</tr>
<tr>
<td>800 to 900</td>
<td>22.7</td>
<td>0.16</td>
<td>5553</td>
<td>0.6</td>
<td>1.81</td>
</tr>
<tr>
<td>700 to 800</td>
<td>23.4</td>
<td>0.11</td>
<td>5416</td>
<td>2.0</td>
<td>1.92</td>
</tr>
<tr>
<td>600 to 700</td>
<td>23.9</td>
<td>0.16</td>
<td>5256</td>
<td>1.6</td>
<td>2.02</td>
</tr>
<tr>
<td>500 to 600</td>
<td>24.7</td>
<td>0.20</td>
<td>5076</td>
<td>1.7</td>
<td>2.16</td>
</tr>
<tr>
<td>400 to 500</td>
<td>25.6</td>
<td>0.27</td>
<td>4859</td>
<td>1.3</td>
<td>2.33</td>
</tr>
<tr>
<td>300 to 400</td>
<td>27.0</td>
<td>0.19</td>
<td>4642</td>
<td>3.3</td>
<td>2.59</td>
</tr>
<tr>
<td>200 to 300</td>
<td>28.8</td>
<td>0.14</td>
<td>4287</td>
<td>2.5</td>
<td>2.99</td>
</tr>
<tr>
<td>100 to 200</td>
<td>31.5</td>
<td>0.08</td>
<td>3629</td>
<td>3.6</td>
<td>3.86</td>
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<tr>
<td>0 to 100</td>
<td>38.0</td>
<td>0.40</td>
<td>1804</td>
<td>11.2</td>
<td>9.36</td>
</tr>
</tbody>
</table>

(4.45 x $10^{-4}$ $\mu$A Cd$^{2+}$ in 0.10 M KCl, drop time = 1.20 sec, at -750 mV, 9.3139 V = 10,000 cts/sec)

$^a$Average of 30 drops used at each gate setting.

$^b$10 µA f. s. I to V converter setting used to obtain background data.
Table III. Reproducibility of Consecutive Sweep on the Same Solution.

<table>
<thead>
<tr>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>642</td>
<td>660</td>
<td>658</td>
<td>29699</td>
<td>29693</td>
<td>29654</td>
</tr>
<tr>
<td>797</td>
<td>797</td>
<td>841</td>
<td>29684</td>
<td>29677</td>
<td>29654</td>
</tr>
<tr>
<td>980</td>
<td>1015</td>
<td>1024</td>
<td>29685</td>
<td>29673</td>
<td>29635</td>
</tr>
<tr>
<td>1163</td>
<td>1167</td>
<td>1141</td>
<td>29672</td>
<td>29670</td>
<td>29634</td>
</tr>
<tr>
<td>1283</td>
<td>1273</td>
<td>1273</td>
<td>29679</td>
<td>29663</td>
<td>29635</td>
</tr>
<tr>
<td>1322</td>
<td>1324</td>
<td>1329</td>
<td>29644</td>
<td>29642</td>
<td>29609</td>
</tr>
<tr>
<td>1292</td>
<td>1283</td>
<td>1285</td>
<td>29657</td>
<td>29650</td>
<td>29586</td>
</tr>
<tr>
<td>1186</td>
<td>1179</td>
<td>1181</td>
<td>29666</td>
<td>29634</td>
<td>29629</td>
</tr>
<tr>
<td>1032</td>
<td>1028</td>
<td>1002</td>
<td>29593</td>
<td>29627</td>
<td>29598</td>
</tr>
<tr>
<td>845</td>
<td>825</td>
<td>803</td>
<td>29634</td>
<td>29626</td>
<td>29603</td>
</tr>
<tr>
<td>667</td>
<td>651</td>
<td>662</td>
<td>29624</td>
<td>29616</td>
<td>29593</td>
</tr>
<tr>
<td>Σ 11,209</td>
<td>11,202</td>
<td>11,199</td>
<td>326,237</td>
<td>326,171</td>
<td>325,861</td>
</tr>
</tbody>
</table>

(total volume: 50 ml; gate: 400 msec, wait 450 msec; open-circuit drop time: 1.02 sec; potential step height ≈ 5 mV)

\(^a^\)Triplicate runs on the same solution: 8.88 \times 10^{-5} \text{ M Ca}, 0.100 \text{ M KCl}.  


FIGURE CAPTIONS

Fig. 1. Digital electrochemical system.

Fig. 2. Potentiostat.

Fig. 3. Digital integrator.

Fig. 4. Limit rate meter.

Fig. 5. Multifunctional voltage ramp generator.

Fig. 6. Drop separation sensor.

Fig. 7. Polarographic programmer.

Fig. 8. Incremental digital differentiator.

Fig. 9. Digital polarographic operation.

Fig. 10. Coulometric titration of lead. 700.7 µg Pb\(^{2+}\) in 0.10 M KCl, sample pretitrated at -200 mV, titrated at -600 mV vs. SCE.

Curve A: 754.0 µg Pb\(^{2+}\) found without normalization.

Curve B: 702.9 µg Pb\(^{2+}\) found with normalization.

Fig. 11. Coulometric titration of Pd\(^{4+}\) in the presence of Pt\(^{4+}\). 0.05 M N\(_2\)\(^{-}\), 0.24 M phosphate buffer, pH 6.85, +0.100 V vs. SCE.

1. Reduction of 4 mg Pd\(^{4+}\) in the presence of 108 mg Pt\(^{4+}\).

2. Reduction of 4 mg Pd\(^{4+}\) in the presence of 54 mg Pt\(^{4+}\).

3. Reduction of 4 mg Pd\(^{4+}\) alone.

Fig. 12. Subtractive polarography. Solution: 1.12 × 10\(^{-6}\) M Cd\(^{2+}\), 1.1 × 10\(^{-7}\) M Pb\(^{2+}\), 0.10 M KCl.

A. Background current plus Cd\(^{2+}\) wave.

B. Background current alone.

C. Cd\(^{2+}\) wave alone after subtractive data transfer of B into A.
Fig. 13. Difference polarogram of Cd$^{2+}$ at $9 \times 10^{-9}$ M level.

Fig. 14. Incremental derivative polarography. Solution: $2.66 \times 10^{-4}$ M Cd$^{2+}$, $3.06 \times 10^{-4}$ M In$^{3+}$, 0.1 M KCl. Scanned from -0.300 V to -0.800 V vs. SCE.

A. $\Delta E = 10$ mV.
B. $\Delta E = 5$ mV.
C. $\Delta E = 2.5$ mV.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 6
Fig. 7
<table>
<thead>
<tr>
<th>A</th>
<th>Drop current I</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>Digital integrator out</td>
</tr>
<tr>
<td>C</td>
<td>Signal gating</td>
</tr>
<tr>
<td>D</td>
<td>Signal sampling</td>
</tr>
<tr>
<td>E</td>
<td>Integral Ramp out</td>
</tr>
<tr>
<td>F</td>
<td>Ramp advance Analyzer channel advance</td>
</tr>
<tr>
<td>G</td>
<td>Memory store Channel</td>
</tr>
<tr>
<td>H</td>
<td>Differential Ramp out Ramp advance</td>
</tr>
<tr>
<td>I</td>
<td>Analyzer channel advance</td>
</tr>
<tr>
<td>J</td>
<td>Analyzer memory sense</td>
</tr>
<tr>
<td>K</td>
<td>Memory store</td>
</tr>
</tbody>
</table>

Fig. 9
Fig. 10
Fig. 13
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