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

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August 1970

The digitizing time-synchronizing current-sampling system presented consists of a collection of function modules. By using a patch panel to interconnect the appropriate modules, it is possible to synthesize most of the instruments useful for electrochemical analysis. All data are recorded in digital form and are thus computer compatible.

Four instruments new to the field of electrochemical instrumentation are described. They are: a digital integrator, using the principle of charge reinjection; an on-line digital differentiator; a charge-rate-sensitive limit rate meter; and a gated base-line restorer.

The studies presented show the versatility of the system. Automation of constant-potential coulometry by the use of a time programmer or the limit rate meter is discussed. Pre-dicative 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 multichannel scaling mode to

distribute data between the various memory channels as a function of time. Subtractive normalization by data processing of the log i -time curves of small samples results in the virtual elimination of the background current contribution, thus improving the accuracy and sensitivity of the titrations.

Polarographic precision is improved by more than an order of magnitude over that obtainable by classical polarography, and the sensitivity is increased to the 10^{-8} M level by the judicious selection of the current-sampling gate width and location during the life of the drop. Polarographic maxima of hydrodynamic origin are eliminated by current sampling at the beginning of the life of the drop. Difference polarography becomes a practical reality through the use of a subtractive transfer of data between memory locations, since the same capillary electrode is used in obtaining the background current scan and the sample scan. This technique normalizes the background and thus improves the diffusion-current measurement and increases polarographic sensitivity to the 5×10^{-9} M level. The ability of the gated base-line restorer to attenuate high continuous background currents while passing small faradaic current pulses generated in an anodic staircase-potential scan increases the sensitivity of the anodic stripping method by permitting use of more sensitive current ranges. Also the time necessary for preconcentration is reduced.

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 (1-5).

The digitizing, time-synchronizing current-sampling system presented here consists of a collection of function modules. By using a patch panel to interconnect the appropriate modules, it is possible 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 or were purchased commercially. Although a pulse-height analyzer, operated in the multichannel scaling mode, 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.

One should note the conspicuous absence of drop-frequency filters, drop knockers, and other familiar equipment usually associated with modern polarography.

The following instruments are new to the field of electrochemical instrumentation: a digital integrator, using the principle of charge reinjection; an on-line digital differentiator; a charge-rate-sensitive limit rate meter, and a gated base-line restorer. In addition, a potentiostat, a current amplifier, a multifunctional ramp generator, a drop-separation sensor, a polarographic timer, an analyzer interface unit, and timers employed in electrochemical studies are discussed.

The studies presented are those which show the versatility of the system. Automation of constant-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^{-8} M level is obtained by the judicious selection of the current-sampling period and location during the life of a drop. Polarographic maxima of hydrodynamic origin can be eliminated by current sampling at the be-

ginning of the life of the drop. Difference 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 5×10^{-9} M level. The ability of the gated base-line restorer to attenuate high continuous background currents while passing small faradic current spikes generated in an anodic stair-step-potential scan increases the sensitivity of the anodic stripping method by permitting the use of more sensitive current ranges, and reduces the time necessary for preconcentration.

INSTRUMENTATION

A block diagram of the digital electrochemical system is shown in Fig. 1. A description of the system begins with the basic instruments needed for coulometric studies--a potentiostat, a current amplifier, and a digital current integrator--and proceeds with a discussion of the auxiliary instruments needed to do polarography. Concepts, not construction details, are presented.

Potentiostat. The potentiostat shown in Fig. 2 is of a conventional design (6) and has output capabilities of ± 100 V at 100 mA. The control amplifier, a Zeltec 140B operational amplifier, is followed by a power complementary emitter-follower in order to deliver high current with good phase stability. The use of three Philbrick P2AU high-impedance differential-input operational amplifiers avoids loading the reference electrode. Either constant-current or constant-potential operation

can be conveniently selected. The range of either of these functions can be controlled locally by a 10-turn helipot or remotely by a multifunctional ramp generator.

Current Amplifier. The current amplifier consists of two M141 Zeltec operational amplifiers; the first is used as a current-to-voltage converter, and the second provides phase inversion for integrator drive upon reversal of the cell output polarity. Zero offset, if needed, is obtained by injecting current into the device's input from a stable potential source.

The Digital Integrator. One of the most critical tasks in electrochemical analysis is that of measuring charge accurately. The development of active analog integrators (7) has resulted in notable improvements in coulometric accuracy, but even with such integrators several problems remain, owing to capacitor hysteresis, drift, linearity, and measuring definition. Our digital approach virtually eliminates these problems.

Figure 3 shows the integrator block diagram. Current flowing into the input of the active integrator produces a charge on C_1 , causing a rise in the output potential of the device. A sensitive differential comparator sensing this output potential detects an increase, opens a gate, and permits the flow of locally developed clock pulses. These pulses trigger an extremely stable and adjustable "one-shot" and current driver, which develop output pulses of a highly accurate time width and amplitude. These impulses of current are used for charge reinjection at the active integrator's input. Charge reinjection continues as long as there is input current flow through R_1 and until C_1 is returned to its initial charge state.

Capacitor C_2 supplies a temporary sump for input charge, permitting a slower correction of input-charge conditions by the active integrator. Linearity and accuracy are thus improved. Integrator readout is accomplished by counting the number of one-shot pulses, either with a digital scaler or in the individual channels of a multichannel analyzer operated in the multichannel scaling mode. Calibration in gram equivalents of oxidation or reduction is possible by proper control of the one-shot timing period.

Several advantages accrue owing to this incremental approach to charge integration. Capacitor hysteresis error is virtually eliminated because of the very small potential excursions permitted across C_1 , and high measuring definition is insured by the 500-kHz digitizing rate available. The integrator is exceptionally linear over a four-decade range and exhibits stability to within less than 0.02% for days. A current amplifier is interposed between the potentiostat and the integrator because of the present integrator's inability to digest more than about 10 mA of input current, owing to limitation in the size of its charge reinjector. Future development of a high-level charge reinjector--perhaps a factor of 100 higher--would eliminate entirely the need for a current amplifier in constant-potential coulometry and polarography.

Limit Rate Meter. This instrument consists of a count-rate meter followed by a potential comparator, a flip-flop, and an output driver. It is sensitive only to descending count rates. To initiate operation, the flip-flop is reset, allowing the output driver to ungate the "accumulate" scaler, which senses the output of the digital integrator.

When the pulse rate drops below a preselected level, the device gates the scaler off. A block diagram is shown in Fig. 4.

Multifunctional Voltage Ramp. Figure 5 shows the essential features of the multifunctional voltage ramp used in making potential 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 ranges from 0.5 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. Figure 6 shows the arrangement used to sense drop separation (8). A source of low-amplitude 250-kHz potential is applied between the auxiliary and working electrodes through capacitor C_1 . The resistor R_1 has an impedance value close to or larger than that of C_1 . As mercury drops separate from the capillary, abrupt changes in cell impedance produce disturbances in the potential distribution between C_1 and the cell, which are amplified and used to trigger a

Schmitt discriminator. Output pulses from this discriminator are used to initiate the polarographic timing interval.

Polarographic Programmer. Timing pulses from the drop-separation sensor, in the case of the DME (dropping mercury electrode), or from an auxiliary time programmer, in the case of solid electrodes, trigger a wait-gate unit which controls the duration and time relationship of the data-sampling intervals relative to the timing pulses. The wait-gate unit, shown in Fig. 7, consists of two one-shots with output drivers. The period of the first one-shot determines delay. The trailing edge of the wait period is used, in turn, to trigger the second "gate" one-shot, which determines the duration of the sampling-gate period.

The wait and gate time intervals are continuously variable from about 1 msec to 1.8 sec. The reproducibility of a 1-second gate period is better than 0.04%.

Digital Differentiation. Derivative polarographic curves can be obtained with a DME or a solid electrode. For the DME the data-acquisition process is initiated by sensing the drop detachment. For solid electrodes an auxiliary timer supplies impulses for initiation of the data-acquisition process. Figure 9 shows how digital differentiation is achieved by first storing subtractively the number of counts obtained with a drop in the first data channel of the analyzer. The cell control potential is then stepped to its next value and the analyzer is instructed to store additively the number of counts obtained from the next drop. Thus a difference in counts is obtained between the two potentials. At the inception of the following drop the memory channel of the analyzer is

advanced one location and the process is repeated. Figure 8 is a block diagram of the digital differentiator.

A wait pulse in the polarographic programmer simultaneously causes triggering of a steering flip-flop and a wait-gate generator located in the digital differentiator. The steering flip-flop provides add-subtract logic commands for the analyzer. "AND" gate 1 furnishes a ramp-advance command output each time a wait signal drives the steering flip-flop to its $\bar{Q}$ state. "AND" gate 2 gives a channel advance command each time the steering flip-flop is in its Q state while the delayed channel-advance pulse, provided by initiation of the wait input, is present. One-shot 1 delays channel advancing in order to avoid interference between add-subtract steering and the analyzer's own channel-advance cycle. One-shot 2 develops channel-advance pulses which feed through "AND" gate 2 when the steering flip-flop is in its Q state. RC slow-down filters inserted in series with the analyzer's add-subtract inputs prevent destruction of information, held in the memory scaler of the analyzer during the add-subtract switching cycle.

Gated Base-line Restorer. This module uses a track-and-store amplifier to supply a base-line restoration signal to the current amplifier. The operation of the module can best be understood by considering the sequence of events occurring during a gated stair-step-potential scan. The track-and-store amplifier is in the track mode during the time in which the initial cell potential is applied. It thus charges up to an output potential necessary for current amplifier output base-line restoration to zero. During the sampling period the track-and-store

amplifier is switched to its hold mode, and during this same period the cell potential is stepped up to its new value. Two signals are sent to the current amplifier during the sample period, one being the inverted output of the track-and-store amplifier, the other being the cell current. If for example, the current at any sampling period were exactly equal to the current before it, then the output potential of the current amplifier would be zero. If, on the other hand, a different current flowed during the following sampling period, then the output of the current amplifier would be proportional to the difference between the currents of the two periods. Thus, one is in effect looking at the small changes in current, occurring at different cell potentials, free of any continuous background current. After each gated sampling period, the track-and-store amplifier is switched to the track mode, is charged to an output potential proportional to the new value of the background current, and is now ready to supply the necessary signal to compensate the current amplifier for the average background current during its next sampling period. The time sequence of these events is shown in Fig. 9. Figure 10 is a block diagram of this module.

Multichannel Pulse-Height Analyzer and Data Processor. A Northern Scientific Model 610 1024-channel pulse-height analyzer, operated in the multichannel 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 precision 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 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 remotely control the duration of the coulometric or polarographic operations. The other supplies simulated drop-separation timing for sample-period advancing when solid or mercury-pool electrode polarography is being performed, and serves as a signal-routing controller when a coulometric titration is being performed.

Two 10^6 -capacity scalers are used as accumulators. Generally, one of these is used; however, it is possible to divide data between the two scalers for selected time periods by aid of the auxiliary timer, and the signal router.

A Mosley X-Y point plotter, equipped with a null detector, is employed to plot out stored digital information from the pulse-height analyzer. Alternatively, stored numerical information can be printed out on paper tape at the rate of 40 lines/sec, by use of the Franklin printer.

A Fairchild Model 7050 digital voltmeter allows continuous visual display of the cell reference-electrode potentials or the current-amplifier 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 amplifier, the integrator, and the digital voltmeter.

A Hewlett-Packard Model 132A Dual-Beam oscilloscope aids in visually examining wait-gate alignment 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 (9), and a conventional DME assembly was employed in conjunction with a ≈ 1 -sec Smoler capillary electrode for polarographic studies. A paraffin-impregnated graphite electrode was constructed, and the procedure described by Matson and co-workers was employed for anodic stripping analysis (10). 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. Constant-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 titrate 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. 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 (5, 11-14). These methods are based on the assumption that the electrolysis current follows Lingane's equation (15),

$$i = i_0 e^{-kt},$$

where i is the current at time t , i_0 is the initial current, and k is the electrolysis constant. If the system under study conforms to this equation, one may calculate the number of coulombs consumed at the titration end point, using the integrated form of Lingane's equation, which was derived by Meites (14).

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

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 scalars. 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 electroreduction 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 calculation of the titration end point. 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 11, 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 gratifying, 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 can be eliminated by the use of an iterative computer program to linearize the data.

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 (16). 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- μ A 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 in 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:

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 Fig. 12). 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. It also provides selected electrogeneration times ranging from continuous operation to 10- μ sec intervals. This feature is very helpful in locating constant-current coulometric titration end points by potentiometry or voltammetry.

DME Polarography. Considerable effort has been made to improve the rather mediocre sensitivity of classical DME polarography. Most of the successful modern analog techniques achieve a high, real sensitivity based on the following observation. In the period just prior to the drop's detachment, the time rate of growth of electrode surface area, at a constant mercury flow rate, is minimal, and the capacitive charging of the electrode double layer is very small. The ratio of faradic to capacitive current is therefore rather favorable. Sample-gating the current during this favorable time interval results in improved sensitivity. Pulse, "Tast", and square-wave polarographic instrumentation make use of this observation of the favorable time

interval. These instruments differ primarily in the way in which the cell potential is varied.

Our system makes use of the above-stated principles, but it is electronically simpler than the foregoing instruments, since there is no need for familiar devices such as drop-time controllers, signal filters, pen-arrest mechanisms, tuned derivative takers, and other equipment generally associated with analog signal recording. The digital record of a polarographic scan is highly amenable to data processing. Important advantages accrue. Figure 1 indicates the modules required for polarography and Fig. 9, lines A through F, shows the time sequence of operation. The staircase voltage ramp shown in Fig. 9E is employed throughout the polarographic studies below, since its use minimizes the capacitive current flow during the current-measuring interval. In order to make best use of the instrument, it is necessary to examine the reproducibility of the counting rate at various sample gate widths, and to determine the effect of the sample gate positioning in the life of the drop upon the signal-to-background ratio. Table I shows the effect the sample gate width has on the precision of current measurement. In view of these data, one should use a gate interval wider than 30 msec, since shorter sampling times result in a decrease of precision, owing to a decrease in the signal averaging of short-term current fluctuation. It is interesting to note that the average relative error of the data for the gated drop, at times greater than 30 msec, is less than that of the ungated drop by a factor of 13.

Table II summarizes the effect the sample gate position has, at constant width, on the signal-to-background ration (S/Bkg) for cadmium. These data permit balancing the improvement in statistics at ever-increasing gate widths (increasing count accumulation) with the continual decrease in the S/Bkg ratio, and thus to select an optimum gate width and location. For a 1-sec drop time, 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 difference polarography (discussed below).

The sensitivity of this method for well-behaved electroactive species, such as lead and cadmium, is about 1×10^{-8} M. Table III shows the reproducibility obtained with cadmium on three consecutive sweeps. These data were taken on the diffusion plateau.

DME Difference Polarography. Potentially, one of the most useful, yet one of the most elusive, approaches to high-sensitivity polarography is difference polarography (17). It would be possible to eliminate entirely the residual current by difference, provided two identical capillary electrodes could be obtained and operated in synchronization under identical instrumental conditions and under separate, but equal, heads of mercury. One electrode would sense residual current in a solution of supporting electrolyte alone, and the other would sense residual current plus faradaic current in a solution of supporting electrolyte containing the sample. The difference between the two signals would be faradaic current alone. In theory, this approach is instru-

mentally simple, but in practice, using analog signal recording, it is complex and requires synchronized drop-time controllers, a balance amplifier, and signal filters, because obtaining two identical capillaries is highly improbable. Our system circumvents all these problems very simply by its ability to record polarographic signals digitally, using the same capillary electrode. To perform difference 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 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 Fig. 13). Traces A, B, and C show the results of these operations for cadmium at the 125-ppb level. Traces A and B were deliberately offset to aid in their display. The small contamination wave (see arrow, Fig. 13) just prior to the cadmium wave was due to the presence of 23-ppb of lead.

Difference 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 2 over that stated above.

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.

Derivative Polarography. The instrumentation required to do derivative polarography is described above. See Fig. 1 and Fig. 9, lines ABC and HIJ. When one considers the way in which our system operates, it is obvious that the shape of the recorded polarogram can only approximate a true derivative. Using analog instrumentation, Auerbach and co-workers have studied this incremental approach to derivative polarography in considerable detail (8). When digital recording equipment is used, it is immaterial whether the derivative is taken concurrently with the scan, as we have done, or after the scan by data processing of the integral polarogram. If electrochemical reaction rates are ignored, the maximum scan rate permitted is limited only by the cycle time of the digital recording device used, and by the digitizing rate of the integrator.

Figure 14 shows the effect of the stair-step potential height on the resolution of 1.15:1 molar concentrations of indium and cadmium whose half-wave potentials are separated by only 50 mV in 0.1 M KCl supporting electrolyte. The resolution improves as the potential step becomes smaller, but even a 10-mV step is sufficient to show that two couples are present.

Table III shows the reproducibility obtained for three consecutive derivative sweeps on cadmium.

Polarographic Maxima. The phenomena of maxima, at the dropping-mercury electrode, have long plagued the field of classical polarography, Levich indicates maxima arise either from electrocapillary motion or from turbulence within the mercury drop, and offers a theoretical explanation based on hydrodynamics (18). Meites has pointed out exceptions to Levich's treatment (19). Analysts have used surface-active organic materials to suppress maxima. Schmid and Reilley studied the effect these materials have on the current-time behavior of a single drop (20). A time delay was observed before the surface-active material affected the electrode process. This delay was inversely related to the concentration of the suppressing agent. These substances might be looked upon as performing a chemical current-time sampling function at the beginning of the life of the drop. Cover and Connery have shown that maxima disappear when one vibrates a DME at a high rate (21). This vibration causes premature detachment of the drop, resulting in a "high rate of surface area formation." We feel that this approach constitutes an electromechanical form of sampling, since current is recorded only during the first part of the life of a drop. Early electronic current gating on a normal DME should also result in the elimination of maxima, provided the maxima are of hydrodynamic origin.

Figure 15A shows a polarogram of nickel in an ammonia buffer, obtained by gating on the last fraction of the life of the drop. The maximum is pronounced. Figure 15B shows the current-time behavior of a drop in the maximum-potential region. The current is normal at the

beginning of the drop, but as the drop grows with time, the current behavior becomes increasingly erratic. If one gates very soon after the birth of the drop, a normal, maximum-free polarogram results (see Fig. 15C). Although our experience is not yet extensive, we feel that the early-gating method holds promise for effectively dealing with the hydrodynamically originated maximum, although at some expense of sensitivity and precision (see Tables I and II), and with some distortion of polarographically irreversible waves.

Consider Figs. 16 and 17, which show polarograms obtained by using the early and late gating techniques. The sensitivity for both nickel and cadmium are decreased by about a factor of 2 on early gating; however, the nickel wave is more drawn out and the half-wave occurs at a more negative potential. In contrast, the cadmium wave is essentially unaffected. These differences for the two ions could be explained on the basis of the large differences in their heterogeneous rate constants. Nickel is polarographically irreversible. A Nernst plot of data obtained by early current sampling on a solution of cadmium at the 2 ppm level, gave a straight line with a slope of 31.6 mV. Reversibility of cadmium, then, is indicated.

Incidental to this study, it was observed that early-gated polarograms are insensitive to stirring. This should promote the use of the DME in amperometric titrations.

Maxima may also arise from disproportionation reactions. Figure 18 shows polarograms of copper in an ammonia buffer. A pronounced maximum results when the current is sampled early in the life

of the drop. Two other polarograms were obtained by sampling during the mid-life (curve 2) and near the end of the life of the drop (curve 3). Figure 19 shows the current-time behavior of the drop in the maximum region. It is interesting that the height of the peak of the maximum is about the same height as the first reduction step. This maximum would be accounted for by the disproportionation reaction

The role surface-active materials play in eliminating this maximum is not obvious. This system deserves further study.

Anodic Stripping. Several problems are attendant on performing conventional anodic stripping analysis. As high a voltage scan rate as is practical is employed, because the peak current height--hence sensitivity--and the scan rate are directly related (22, 23), but unfortunately the background current also increases with higher scan rates owing to the double-layer charging requirements of the electrode. Too high a scan rate results in severe tailing and loss of resolution between adjacent stripping peaks, since a finite time is necessary for the establishment of amalgam equilibrium at the electrode surface. The peak-height measurement must be made by extrapolation of a generally nonlinear baseline, for accumulation of impurities in the mercury increases the background current relative to a blank scan, owing to a decrease in the hydrogen overvoltage of the electrode (23).

Our instrumental approach eliminates these problems and improves the sensitivity of the method while decreasing the time necessary

for the accumulation step via the gated base-line restorer module. The same instrumentation required for polarography is used for solid electrode voltammetry, but with this difference: the second time programmer now provides the signal to initiate the operation of the system at selected time intervals, thus replacing the drop-separation sensor. The gated base-line restorer permits attenuation of the continuous background current while passing small current changes of short time duration, allowing the use of more sensitive current-amplifier ranges. See Fig. 1. Figure 9, lines G, K, L, and M, shows the time sequences involved. The stair-step ramp is employed to effect potential scanning. The step height used is usually 5 to 10 mV, and the step width is generally 500 msec to give a better signal averaging of the continuous background current stored by the store amplifier in the gated base-line restorer. A 5-msec wait period followed by a gate interval of 100 msec is sufficient to record essentially all of the faradaic current at the solution resistance levels encountered. These instrument settings have an effect on the shape of the stripping polarogram recorded. The height of the stripping peak is related to the potential step height and, in the absence of base-line restoration, the magnitude of the background current depends upon the step width.

Figure 20A shows a stripping polarogram of 0.10 M KCl adjusted to pH 4.0 with HCl. Observe the sharp increase of anodic current as the cell potential decreases. This is due to a decrease in the electrolysis of hydrogen ion. Elements giving waves prior to reaching the plateau would be difficult to detect and measure, because of the nonlinearity of

of the background. Figure 20B shows a repeat of the same experiment, but now using the gated base-line restorer. The high continually changing background present at more negative potentials in the first trace is now absent. The bowing of the base line is due to the changing capacitive charge requirements of the electrode about the electro-capillary maximum potential. These requirements are of a short-term nature, and are generated by the abrupt stair-stepping of the potential. Although the base line is not strictly linear, measurement of the peak area is improved.

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FOOTNOTE AND REFERENCES

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Table I. Effect of gate width on precision. (50 ppm Cd^{2+} 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, $9.3139 \text{ V} = 10\,000 \text{ cts/sec}$).

Gate width, (msec)	Counts/drop ^a	Av deviation, counts/drop	Relative error
10	565	0.6	0.11
30	1828	1.3	0.07
50	3150	0.5	0.02
100	6153	0.2	0.03
200	12377	3.0	0.02
300	17659	4.2	0.02
400	23189	6.9	0.03
600	34560	11.2	0.03
800	44350	17.0	0.04
Ungated	57836	194.0	0.34

^a Average of 30 drops.

Table II. Effect of gate location on sensitivity. (50 ppm Cd in 0.10 M KCl, drop time = 1.20 sec, at -750 mV, 9.3139 V = 10 000 cts/sec).

Gate interval (msec)	Cts ^a bkg. $\times 10^b$	$\frac{\text{Cts}}{\text{av dev}}$	Cts Cd ^a	$\frac{\text{Cts}}{\text{av dev}}$	$\mu\text{g Cd for}$ (S/bkg) = 1
1000 to 1100	22.0	0.17	5840	1.8	0.188
900 to 1000	22.4	0.14	5673	3.9	0.197
800 to 900	22.7	0.16	5553	0.6	0.204
700 to 800	23.4	0.11	5416	2.0	0.216
600 to 700	23.9	0.16	5256	1.6	0.227
500 to 600	24.7	0.20	5076	1.7	0.243
400 to 500	25.6	0.27	4859	1.3	0.262
300 to 400	27.0	0.19	4642	3.3	0.291
200 to 300	28.8	0.14	4287	2.5	0.336
100 to 200	31.5	0.08	3629	3.6	0.434
0 to 100	38.0	0.40	1804	11.2	1.052

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

^b 10 μA f. s. I-amplifier setting used to obtain background data.

Table III. Reproducibility of consecutive sweeps on the same solution (total volume: 50 ml; gate: 400 msec, wait 450 msec; open-circuit drop time: 1.02 sec; potential step height ± 5 mV).

Polarograms					
Derivative ^a			Integral ^a		
Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
642	660	658	29 699	29 693	29 654
797	797	841	29 684	29 677	29 654
980	1015	1024	29 685	29 673	29 635
1 163	1 167	1 141	29 672	29 670	29 634
1 283	1 273	1 273	29 679	29 663	29 635
1 322	1 324	1 329	29 644	29 642	29 609
1 292	1 283	1 285	29 657	29 650	29 586
1 186	1 179	1 181	29 666	29 634	29 629
1 032	1 028	1 002	29 593	29 627	29 598
845	825	803	29 634	29 626	29 603
667	651	662	29 624	29 616	29 593
Σ 11 209	11 202	11 199	326 237	326 171	325 861

^aTriPLICATE runs on the same solution: 8.88×10^{-5} M Cd, 0.100 M KC1.

FIGURE LEGENDS

- Fig. 1. Digital electrochemical system.
- Fig. 2. Potentiostat.
- Fig. 3. Digital integrator.
- Fig. 4. Limit rate meter.
- Fig. 5. Multifunctional ramp generator.
- Fig. 6. Drop separation sensor.
- Fig. 7. Polarographic programmer.
- Fig. 8. Digital differentiator.
- Fig. 9. Digital polarographic operation.
- Fig. 10. Gated base-line restorer.
- Fig. 11. Coulometric titration of lead. 700.7 μg Pb in 0.10 M KCl, sample pretitrated at -200 mV, titrated at -600 mV vs SCE.
- Curve A: 754.0 μg Pb found without normalization.
- Curve B: 702.9 μg Pb found with normalization.
- Fig. 12. Coulometric titration of Pd^{4+} in the presence of Pt^{4+} . 0.05 M N_3^- , 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. 13. Difference polarography. Solution: 125 ppb Cd^{2+} , 23 ppb Pb^{2+} , 0.10 M KCl.
- A. Background current plus Cd wave.
 - B. Background current alone.
 - C. Cd wave alone after subtractive data transfer of B into A.

Fig. 14. Derivative polarography. Solution: 2.66×10^{-4} M Cd^{2+} , 3.06×10^{-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. 15A. Late gated polarogram of Ni^{2+} . Supporting electrolyte 1 M NH_3 , 1 M NH_4Cl , 8.8 ppm Ni^{2+} . Wait, 580 msec; gate, 100 msec.

Fig. 15B. Current-time behavior of Ni^{2+} at -1.101 V vs SCE. Supporting electrolyte: 1 M NH_3 , 1 M NH_4Cl , 8.8 ppm Ni^{2+} .

Fig. 15C. Early gated polarogram of Ni^{2+} . Supporting electrolyte: 1 M NH_3 , 1 M NH_4Cl , 8.8 ppm Ni^{2+} . Wait, 3 msec; gate, 100 msec.

Fig. 16. Effect of early or late gating on Ni^{2+} . Solution: 44 ppm Ni, 0.10 M NaClO_4 .

A. Conditions: gate width = 100 msec., gate closed at 95% of drop life at -1.400 V vs SCE. Drop time at -1.400 V = 740 msec.

B. Conditions: gate width = 100 msec., gate opened after 8-msec wait.

Fig. 17. Effect of early or late gating on Cd^{2+} . Solution: 50 ppm Cd, 0.10 M KCl.

A. Conditions: gate width - 100 msec, gate closed at 95% of drop life at -0.900 V vs SCE. Drop time at -0.900 V = 900 msec.

B. Conditions: gate width = 100 msec, gate opened after 8-msec wait.

Fig. 18. Effect of gate positioning on Cu^{2+} . Solution: Cu^{2+} , 10 ppm., 0.1 M NH_3 /0.1 M NH_4Cl , pH 10.6. 200-msec constant gate interval.

1. 8-msec wait.
2. 400-msec wait.
3. 700-msec wait.

Fig. 19. Current-time behavior of Cu at 0.650 V vs SCE.

Fig. 20. Anodic stripping voltammogram of 23-ppb Pb^{2+} . Solution: 0.10 M KCl, pH 4.0. Conditions: Accumulation time, 15 min; step width, 500 msec; step height, 5 mV.

- A. Gated base line restorer out.
- B. Gated base line restorer in.

Fig. 1

Fig. 2

Fig. 3

XBL7010-4006

Fig. 4

Fig. 5

XBL7010-4005

Fig. 6

Fig. 7

XBL7010-4009

Fig. 8

XBL7010-4003

Fig. 9

XBL7010-3949

Fig. 10

XBB 7010-4823

Fig. 11

XBB 7010-4822

Fig. 12

XBB 7010-4824

Fig. 13

XBL 7010-4831

Fig. 14

XBB 7010-4829

Fig. 15a

XBB 7010-4828

Fig. 15b

XBB 7010-4825

Fig. 15c

Ni

XBB 7010-4820

Fig. 16

XBB 7010-4827

Fig. 17

XBB 7010-4826

Fig. 18

0.2 0.4 0.6 0.8 1.0

Sec

XBB 7010-4830

Fig. 19

XBB 7010-4821

Fig. 20

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