

A.C. Polarography Employing Operational Amplifier Instrumentation

Evaluation of Instrument Performance and Application to Some New A.C. Polarographic Techniques

DONALD E. SMITH

Department of Chemistry, Northwestern University, Evanston, Ill.

► This report is concerned with results of an evaluation of the performance of a.c. polarographic instrumentation employing operational-amplifier circuitry and with adaptation of this instrumentation to some new a.c. techniques. Steps useful in obtaining "high performance" a.c. polarographic instrumentation are discussed. An instrument employing tuned amplifiers and an oscillator of high frequency stability yields excellent performance. Reproducibility of $\pm 0.4\%$ relative standard deviation is found for fundamental-harmonic current-amplitude measurements and $\pm 0.8\%$ for phase-angle determinations. Comparable results are observed for second-harmonic measurements. Performance characteristics are graphically illustrated. Previously unreported a.c. techniques, automatic recording of phase angles, and phase-selective detection of second-harmonic currents are discussed with respect to their potential application in trace analysis and basic electrochemical studies. Experimental results obtained with these techniques are given together with appropriate circuitry. Additional instrumental improvements are considered.

APPLICATION of operational amplifier circuitry to a.c. polarography and related techniques is a natural extension of its use in d.c. methods (4, 8, 12). This approach to a.c. instrumentation has been utilized with success in measurement of a.c. polarographic fundamental (10, 26, 27, 30, 35, 36), second (30), third and fourth (16) harmonic current components, phase angles between fundamental harmonic current and applied alternating potential (26, 27), the resistive component of the fundamental harmonic (phase-selective a.c. polarography) (10, 27, 29), and in square-wave polarography (9, 36).

Advantages of operational-amplifier circuitry, such as versatility and reduction of problems associated with ohmic series resistance, are recognized widely. On the other hand, limited band pass of

operational amplifiers limits usable frequencies and the large number of active circuit elements introduce significant noise levels. Such factors will limit the applicability of a.c. polarographic instrumentation based on operational amplifiers. Despite the variety of application, no detailed assessment of the instrument performance and range of application in a.c. methods has been presented. Results of such an investigation comprise some of the material presented here.

Although numerous variations of the a.c. polarographic method (such as those cited above) have been investigated, all possible extensions have not been exploited. Among the untried techniques are automatic recording of a.c. polarographic phase angles and phase-selective detection of second-harmonic currents. Both methods may be of use in analytical work and basic electrochemical studies. Coincident with the investigation of instrument performance, the possibility of adapting standard operational-amplifier circuitry to such measurements has been examined. Results of these studies also are given here.

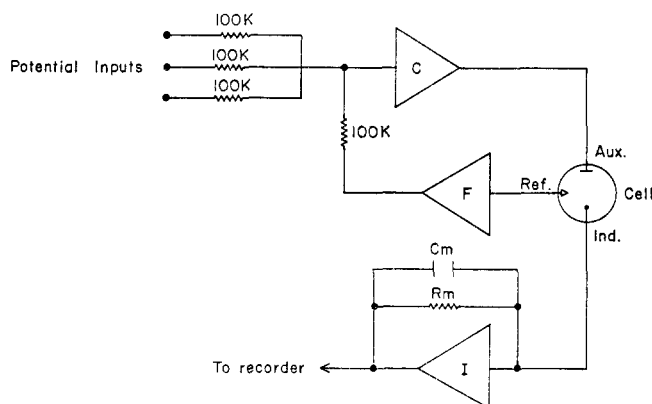


Figure 1. Schematic of operational amplifier controlled-potential configuration

Amplifiers I and C—Philbrick USA-3's suitably biased to eliminate d.c. offset
Amplifier F—Philbrick K2-W, K2-P in DeFord follower configuration (8)
All resistors shown are 0.1% precision, low inductance, wire wound
Cm—damping condensor

EXPERIMENTAL

All operational amplifiers employed were manufactured by G. A. Philbrick Researches, Inc. Specific models are indicated below. A Tektronix Model 502 oscilloscope was used to monitor a.c. signals, measure signal amplitudes, phase angles etc. A Tektronix Model C-13 oscilloscope camera was used to photograph scope traces. All polarograms were recorded on a Sargent Model SR recorder. A Hewlett-Packard Model 202A function generator served as source of sinusoidal potentials in some experiments. A Sargent Model S-29390 polarographic cell was thermostated at $25.0^\circ \pm 0.02^\circ$ C. with the aid of a Sargent S-84810 water bath and a S-71565 liquid circulating pump. Principles of operation and further details of much of the instrumentation are discussed elsewhere (4, 8, 12, 19, 27, 35).

INSTRUMENT PERFORMANCE

A controlled-potential configuration based on operational amplifiers commonly employed in d.c. methods is illustrated in Figure 1. In principle, application of this circuit to fundamental-harmonic a.c. polarography may be accomplished simply. A small-amplitude sinusoidal potential is ap-

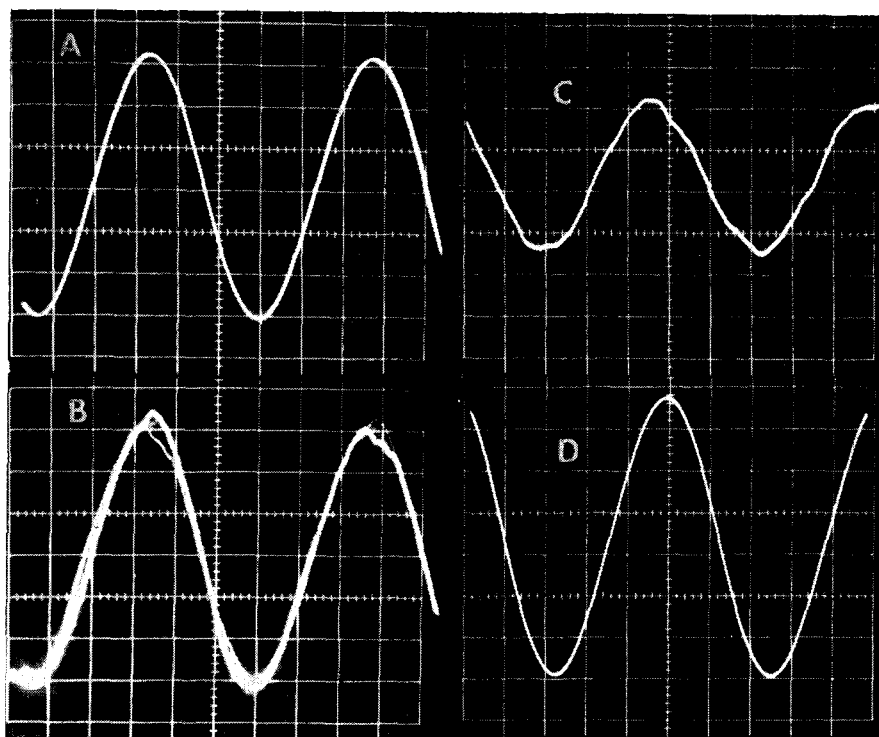


Figure 2. A.C. signals at various points in instrument

- All signals 40 c.p.s.
- (A) Sinusoidal potential signal from oscillator. Scope sensitivity: 2 mv. per cm.
 - (B) Alternating potential signal observed at output of follower. Scope sensitivity: 2 mv. per cm.
 - (C) Alternating current signal observed at output of *I* amplifier. Scope sensitivity: 50 mv. per cm.
 - (D) Alternating current signal after tuned amplification. Scope sensitivity: 2 volts per cm.

plied at one of the potential inputs together with the d.c. scan potential. The current signal (output of Amplifier *I*) is passed through a high pass filter to eliminate the d.c. current component and the a.c. signal is made suitable for recording by rectification and filtering (low pass). An a.c. polarograph so constructed will perform well with no serious problems apparent from qualitative examination of the a.c. polarogram. However, noise levels may introduce serious difficulty in many applications. The magnitude of the noise problem is illustrated in Figures 2A, B, and C. Despite the "clean" a.c. signal source (Figure 2A), the a.c. potential actually applied, observable at output of the follower amplifier, shows considerable noise (Figure 2B). The distorted applied potential, compounded by noise in amplifier *I*, yields the current signal shown in Figure 2C. Thus, significant error may result from assuming that an a.c. polarogram obtained under these conditions represents the fundamental-harmonic a.c. polarographic current which can be related to theoretical equations for purposes of basic electrochemical studies. The influence of such noise levels on phase-angle measurements and trace analysis applications is prohibitive.

To obtain fundamental-harmonic a.c. polarograms undistorted by effects of extraneous a.c. signals (including higher

harmonic faradaic components), and to make possible phase-angle and higher-harmonic faradaic current measurements, highly tuned amplifiers (Figure 3A) were introduced as an integral part of the a.c. instrument (16, 26, 27, 29, 30). Typical response curves for such tuned amplifiers are shown in Figure 4. These curves were obtained with 1% components in the twin-T network without further trimming. Figure 5 shows efficiency with which a two-stage, tuned amplifier selectively amplifies a small second-harmonic component. *Q* values (angular frequency divided by bandwidth) exceeding 10^3 may be realized with one stage although values of about 500 are more typical when 1% components are employed. Output of the tuned amplifier shows negligible noise, as seen in Figure 2D. However, careful examination of tuned amplifier output employing a dummy cell (to obtain constant cell impedance) will show significant instrument instability unless an oscillator of good frequency stability is employed. This requirement is due to the sharp frequency dependence of instrument response introduced by tuned amplification. Relatively small variations in oscillator frequency will lead to significant changes in the output of the tuned amplifier. Demands on oscillator stability depend on *Q* values of the tuned circuit. Larger *Q* values require better

stability. With tuned amplifiers used in this work, short- and long-term oscillator frequency stability of 1 part in 10^4 or better is desirable.

An oscillator with sufficient frequency stability may be obtained conveniently by minor modification of a tuned amplifier as shown in Figure 3B. This oscillator will be referred to hereafter as the twin-T oscillator. A discussion of this type oscillator is given elsewhere (14). The value of capacitor in the positive feedback path (Figure 3B) is adjusted to the minimum value required to yield sustained oscillation. This results in a sine wave of minimum distortion and excellent frequency stability. The short term frequency stability lies in the range of 1 part in 10^4 to 1 part in 10^5 . Long term stability (per hour) appears comparable. A comparison of schematics in Figure 3 shows the operational amplifier-twin-T combination can serve a dual purpose with a simple switch enabling selection of oscillator or tuned amplifier modes of operation. Some other operational-amplifier oscillators of comparable stability are described in the literature (19, 22).

The importance of oscillator-frequency stability is illustrated in Figures 6 and 7. These experiments were run with oscillator frequency corresponding to the sharply rising portion of the tuned amplifier response curve, thus deliberately enhancing effects of oscillator frequency instability. Figure 6 compares signal amplitude stability observed using the twin-T oscillator and a commercial oscillator of lower frequency stability utilizing a dummy cell. Figure 7, A and B, shows phase-angle stability under similar conditions. The latter are results of a 1-minute time exposure of the linear Lissajous pattern observed when current and potential signals are in phase. Width of the pattern indicates phase-angle fluctuations in the 1-minute period. Oscilloscope sensitivity was such that only the middle one-tenth of the pattern is shown—i.e., scope sensitivity is 10 times larger than required for diagonal line to fill the screen. Under these conditions the range of fluctuations observed with the commercial signal generator are approximately 30 to 40 minutes of a degree. The excellent stability of the instrument employing the twin-T oscillator is apparent from Figures 6 and 7.

Polarograms obtained with this instrument are characterized by excellent reproducibility. A typical fundamental-harmonic a.c. polarogram is shown in Figure 8. Reproducibility of a.c. polarograms is illustrated in Figure 9, showing superposition of four successive runs of the same a.c. polarogram at a dropping mercury electrode, utilizing a low pass filter to eliminate drop oscillations from

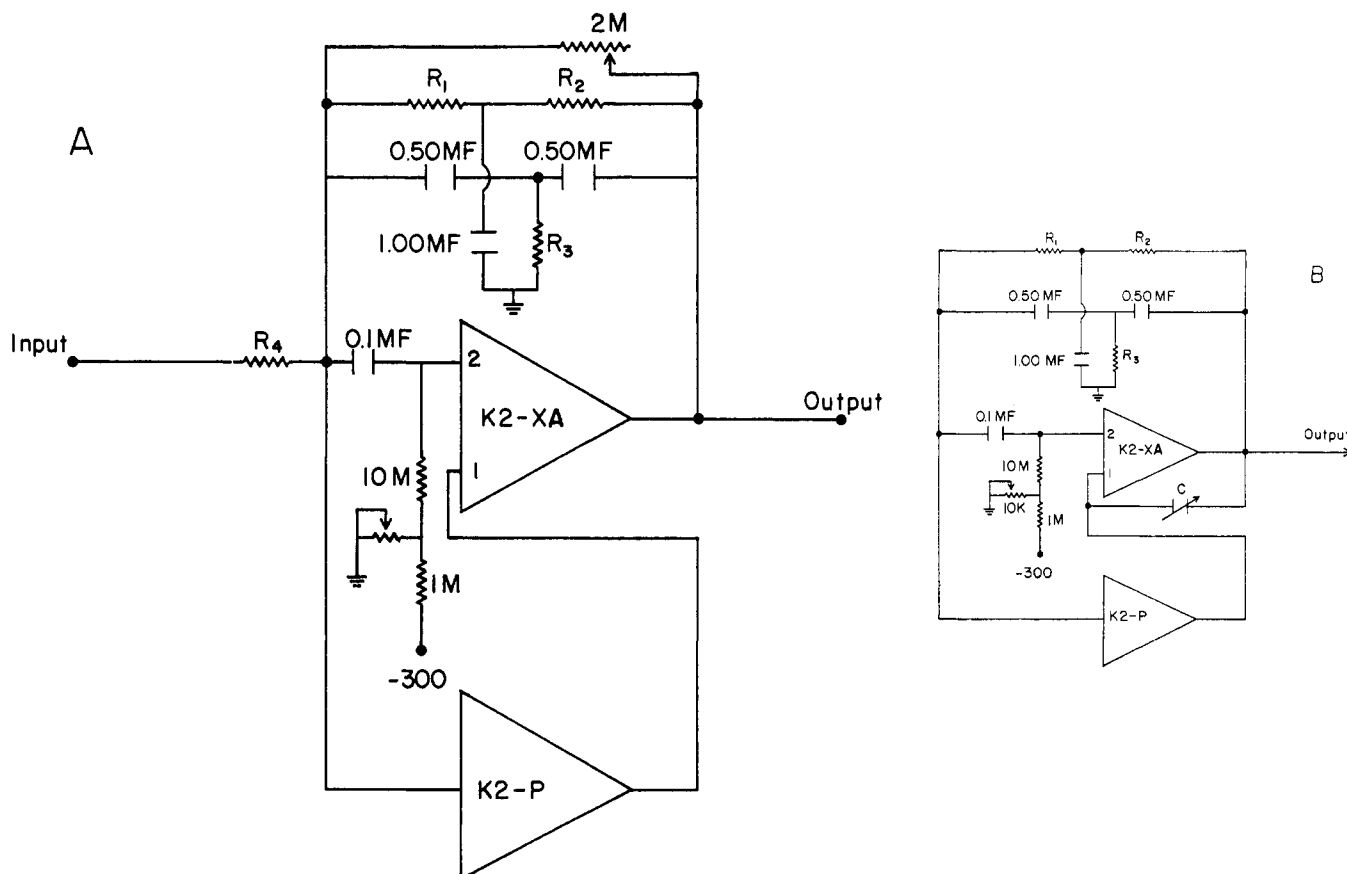


Figure 3. Schematic diagrams

(A) Single-stage stabilized tuned amplifier

(B) Twin-T oscillator

1% precision components employed in twin-T network. All other components 5% precision.
 $R_1 = R_2 = 2R_3 = 3.18 \times 10^6 / f_0$; f_0 = resonant frequency

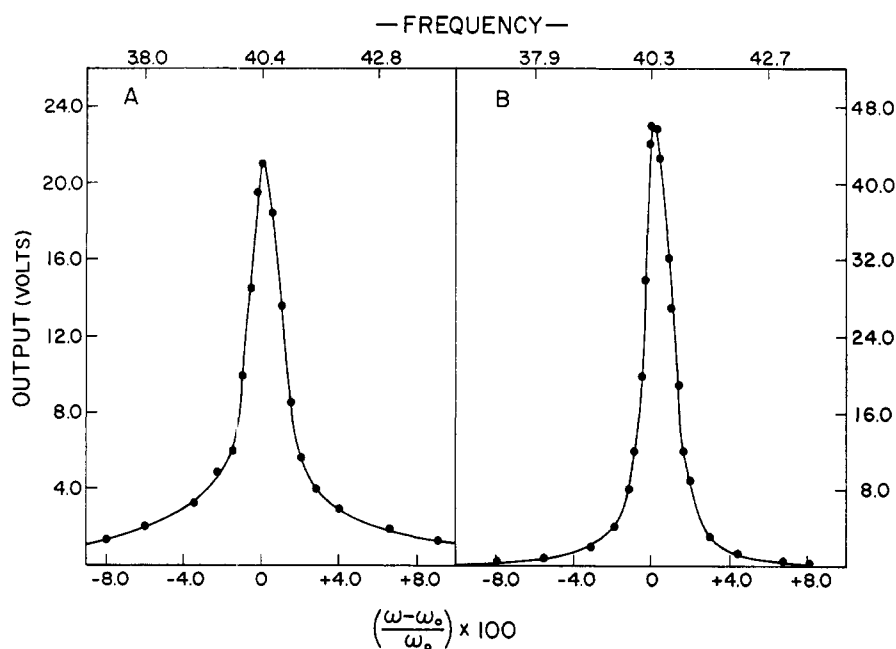


Figure 4. Response curves of tuned amplifiers

(A) Single stage

(B) Two-stage

Input signal 0.200 volt (peak-to-peak)

the recording. Time elapsed from start of first run to end of fourth run was 1 hour. If desired in kinetic studies, a.c. polarograms can be obtained employing very small amplitude alternating potentials with only slight

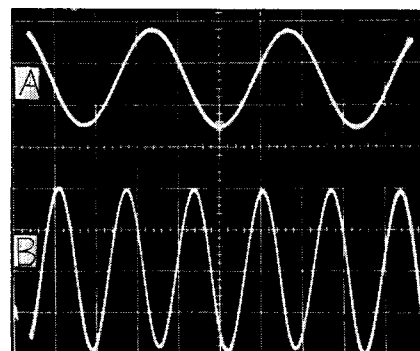


Figure 5. Selective amplification of second harmonic by tuned amplifier

(A) Input signal: 160 c.p.s.; 2% second harmonic distortion. Scope sensitivity: 50 mv. per cm.

(B) Output signal: 320 c.p.s. Scope sensitivity: 2 volts per cm.

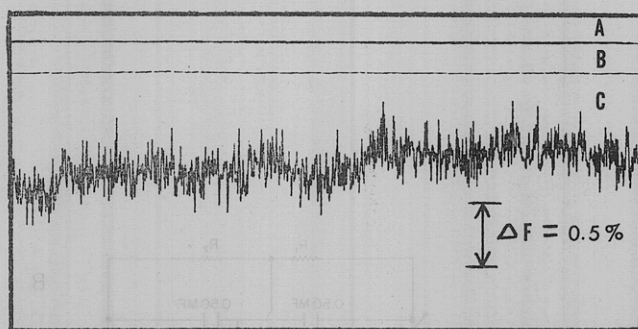


Figure 6. Amplitude stability of instrument

Recorded with dummy cell (constant impedance)
Applied: 10 mv. peak-to-peak, 160 c.p.s.
Recording time: 4 minutes

- (A) With twin-T oscillator: dummy cell impedance, 1000 ohms
(B) With twin-T oscillator: dummy cell impedance, 100,000 ohms
(C) With commercial oscillator (short term frequency stability approximately 0.4%): dummy cell impedance, 1000 ohms

Output fluctuation of magnitude indicated by arrows due to frequency change (ΔF) of 0.5% as calculated from tuned amplifier response curves

evidence of noise as shown in Figure 10. Some second-harmonic a.c. polarograms are shown in Figures 11 and 12. Employing a dropping mercury electrode, tests of reproducibility of a.c. polarographic peak heights indicate a relative standard deviation of $\pm 0.4\%$ for fundamental-harmonic measurements (normal and phase selective) and $\pm 0.6\%$ in second-harmonic measurements. Phase-angle determinations show a relative standard deviation of $\pm 0.8\%$ in evaluation of cotangent of phase angle between total cell current and applied alternating potential. These results are based on experiments employing the systems $3 \times 10^{-3}M$ Cd^{+2} in $1.0M$ sodium sulfate and $3 \times 10^{-3}M$ Fe^{+3} in $0.5M$ sodium oxalate. Experimental frequencies ranged from 10 to 1000

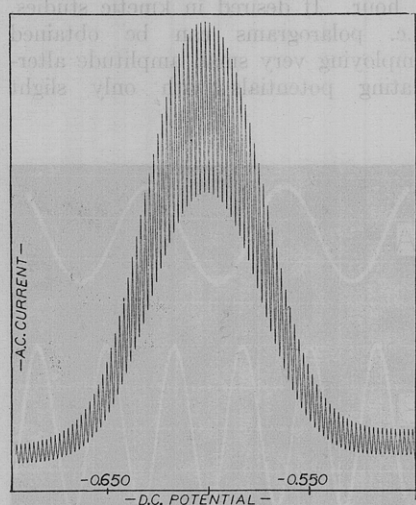


Figure 8. Fundamental-harmonic a.c. polarogram

System: $3 \times 10^{-3}M$ $Cd(II)$, $1.0M$ Na_2SO_4 (A)
Applied: 10 mv. peak-to-peak, 320 c.p.s.
Measured: 320 c.p.s. component, ordinate uncalibrated, d.c. scan rate: 25 mv. per minute

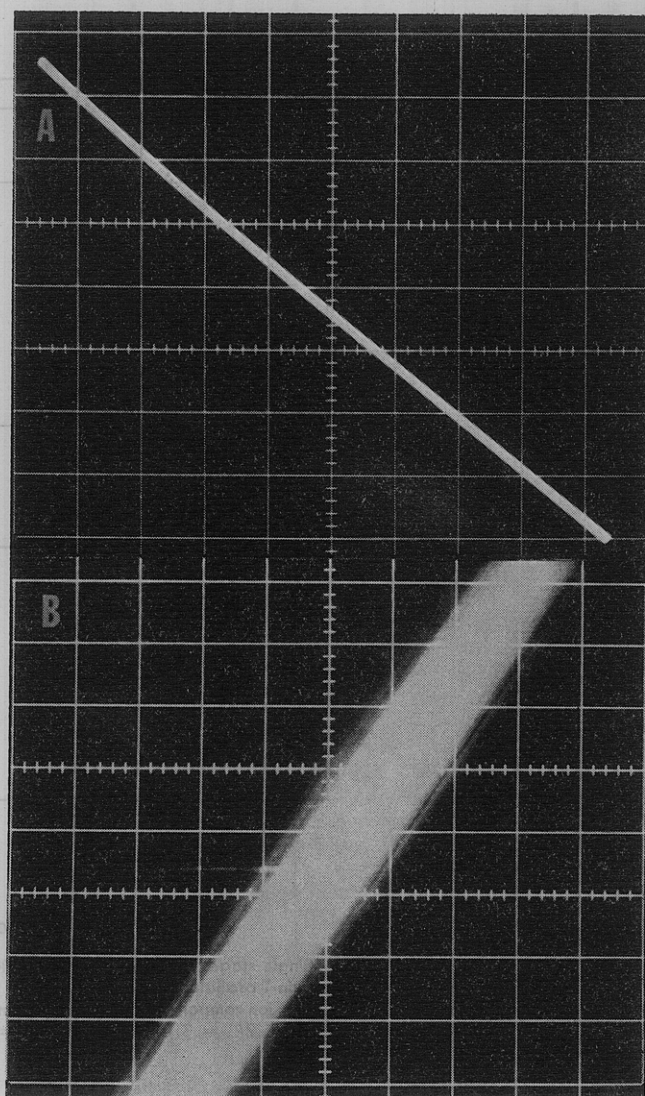


Figure 7. Phase-angle stability of instrument

Recorded with dummy cell
Applied: 10 mv. peak-to-peak, 160 c.p.s.
Dummy cell impedance: 1000 ohms
Exposure time: 1 minute

- (A) With twin-T oscillator
(B) With commercial oscillator

c.p.s. with amplitudes of 10 to 12 mv. peak-to-peak.

Evaluation of accuracy of current and phase-angle measurements was made utilizing a dummy cell consisting of a simple RC circuit of precision components, the least precise of which were $\pm 1\%$ capacitors. Alternating current amplitude and phase-angle determinations were compared with theoretical values calculated from known values of resistors and condensers comprising the dummy cell. Values measured with the instrument agreed with calculated values to well within the 1% tolerance of condensers in the dummy cell and measuring circuit. Methods whereby instrument response is calibrated to yield absolute values of cell current and phase angle were described previously (27, 30).

Regarding frequency response, the present instrument yields excellent performance with small amplitude potentials up to 1000 c.p.s. in aqueous solutions. With a 10 mv. peak-to-peak applied alternating potential, slight loss in control is apparent at 2000 c.p.s. manifested as cell-impedance dependent attenuation of the potential signal observed at output of the follower. Further study of the exact origin of this loss of control has not been undertaken. It can be stated only that the minimum upper limit of applicability of the instrument is 1000 c.p.s. In higher resistance nonaqueous solvents, the upper limit should be somewhat less than 1000 c.p.s. A more detailed critique on frequency characteristics of commonly employed operational amplifiers is given elsewhere (13). Limited

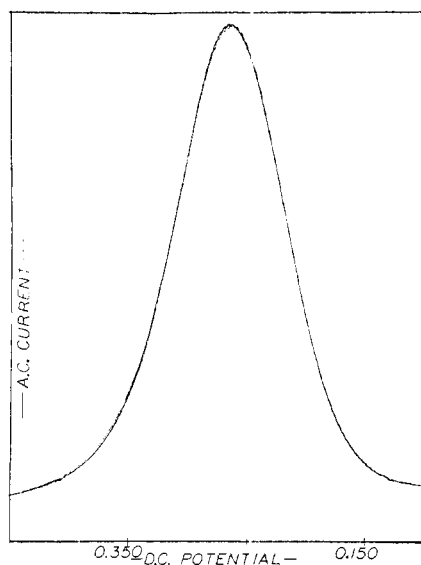


Figure 9. Reproducibility of fundamental-harmonic a.c. polarograms at dropping mercury electrode

System: $3 \times 10^{-3}M$ Fe(III), 0.50M $Na_2C_2O_4$
 Applied: 10 mv. peak-to-peak, 80 c.p.s.
 Measured: 80 c.p.s. component employing long time constant readout to eliminate drop oscillations. Ordinate uncalibrated. Shows four successive runs
 D.C. scan rate: 50 mv. per minute

frequency range remains a handicap in the use of operational amplifiers in a.c. techniques.

PHASE-SELECTIVE SECOND HARMONIC A.C. POLAROGRAPHY

Phase-selective a.c. polarography (10, 11, 15, 27, 29, 32) and second-harmonic a.c. polarography (1, 2, 7, 30) have been suggested as techniques potentially useful in trace analysis and high-frequency kinetic studies because they discriminate against current contributions arising from the double-layer charging process. The former takes advantage of phase-angle differences between faradaic and nonfaradaic currents, while the latter makes use of much greater nonlinearity associated with faradaic processes relative to nonfaradaic processes. A technique taking advantage simultaneously of both distinctions between faradaic and nonfaradaic processes would be phase-selective second-harmonic a.c. polarography. Employing minor additions to the apparatus employed in work described above, phase-selective second-harmonic a.c. polarograms may be obtained. Some examples are given in Figures 11 and 12, together with conventional second-harmonic polarograms.

Theory of the nonfaradaic impedance accounting for nonlinearity (25) leads to expectation of second-harmonic currents due to the double-layer charging process. Such currents represent a limitation to

conventional second-harmonic measurements in trace analysis and in high frequency applications. Application of the theories of Senda and Delahay (25) and Tachi and Senda (31) indicates that the nonfaradaic component will be 45° out of phase with one faradaic second-harmonic peak and 135° out of phase with the other if charge transfer is diffusion controlled (reversible) and adsorption effects negligible. Measurement of the current component quadrature to the nonfaradaic component affords maximum discrimination against the latter. Because the faradaic component quadrature to the charging current component is identical for phase differences of 45° and 135° , efficiency of discrimination will be the same for both peaks. Normal phase-sensitive detectors will respond to the 180° phase difference between faradaic peaks by yielding current deflections of opposing sign. A phase-selective second-harmonic a.c. polarogram with a reversible process should assume the form of a second derivative of the d.c. polarogram (16, 31).

Phase angle relations for faradaic processes controlled by steps in addition to diffusion or for nonfaradaic processes in which adsorption plays a significant role will differ from the simple case considered above. However, a significant difference in phase angles will usually exist between faradaic and nonfaradaic components enabling effective phase discrimination.

Potential advantage of phase-selective detection of second-harmonic currents in high-frequency kinetic studies is found not only in the expectation of

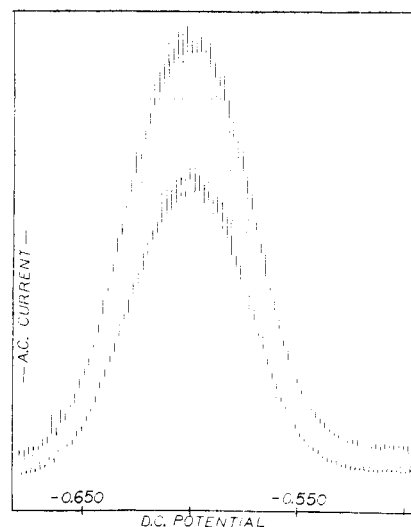


Figure 10. Fundamental-harmonic a.c. polarogram at very small amplitude

Conditions identical to Figure 8 except amplitude applied a.c. potential = 0.20 mv.

low charging-current contributions. Second-harmonic theory of the faradaic process for systems kinetically controlled by diffusion and charge transfer (the quasi-reversible case), while conveniently derived, proves cumbersome in form (20). Phase-selective detection, allowing independent measurement of sine and/or cosine components of second harmonic current, permits application of somewhat less complicated mathematical expressions than required for data based on measurements of total second harmonic.

A schematic of the instrument employed for phase-selective detection of

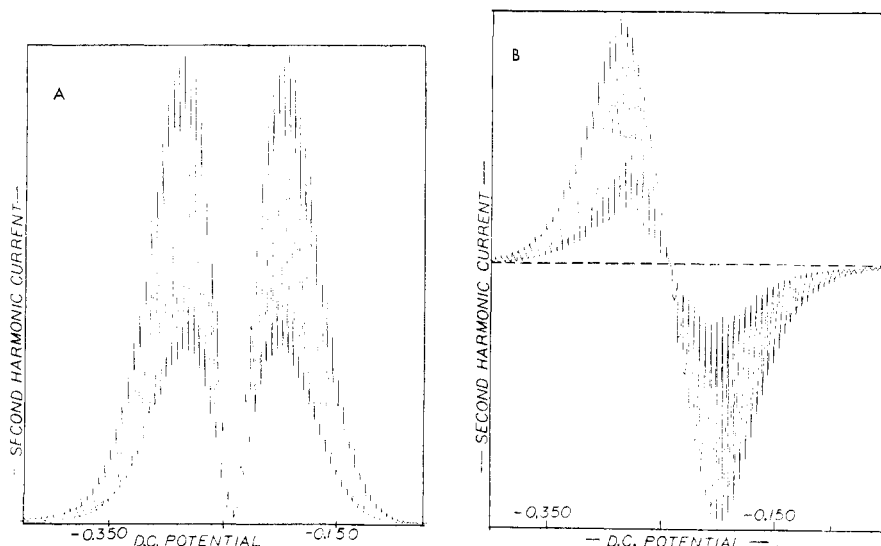
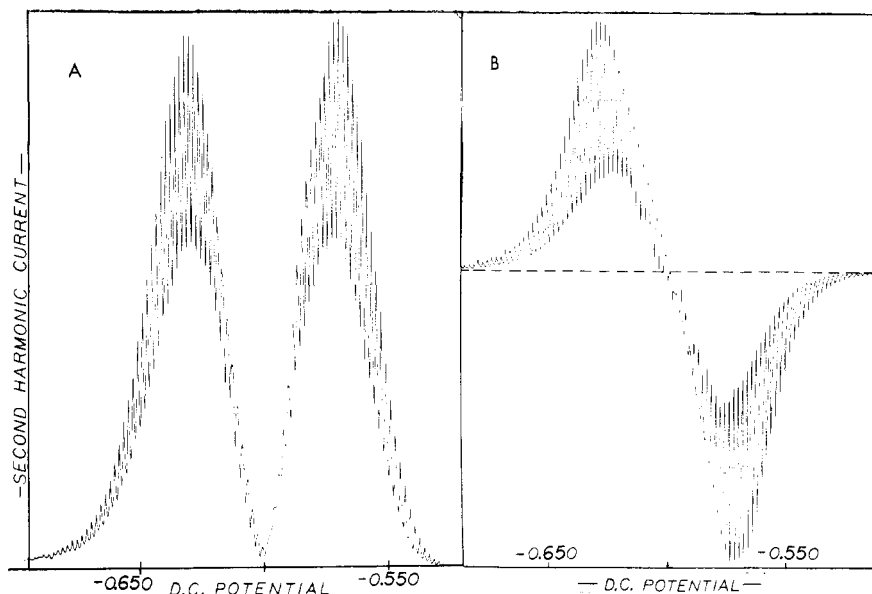


Figure 11. Second-harmonic a.c. polarograms with Fe(III)

System: $3 \times 10^{-3}M$ Fe(III), 0.50M $Na_2C_2O_4$
 Applied: 160 c.p.s., 10 mv. peak-to-peak
 Measured: 320 c.p.s. component, ordinate uncalibrated
 D.C. scan rate: 50 mv. per minute

(A) "Conventional" second harmonic a.c. polarogram
 (B) Phase-selective second harmonic a.c. polarogram



System: $3 \times 10^{-3}M$ Cd(II), 1.0M Na₂SO₄
Applied: 80 c.p.s., 10 mv. peak-to-peak
Measured: 160 c.p.s. component, ordinate uncalibrated
D.C. scan rate: 25 mv. per minute

(A) "Conventional" second harmonic a.c. polarogram
(B) Phase-selective second harmonic a.c. polarogram

second-harmonic currents is given in Figure 13. This instrument differs from one employed in phase-selective detection of fundamental harmonics (27, 29) by addition of components necessary to synthesize a second-harmonic reference signal. Amplification (tuned amplifier 2) and full-wave rectification of the fundamental-harmonic potential signal derived from the follower amplifier generates the desired second-harmonic reference signal which is freed from other harmonics and further amplified by tuned amplifier 3. The second-harmonic current signal is obtained in the usual manner (1, 2, 30), by selective amplification of the current signal (tuned amplifier 4). The phase detector provides a d.c. output proportional to amplitude of current input and cosine of phase angle between reference and current inputs. The phase shifter permits control of phase of reference signal through 360° , making possible compensation for extraneous phase shift in tuned amplifiers etc. and selection of optimum phase relations between reference and current signals. Tuned amplifier 1 serves to eliminate harmonic distortion from alternating potential input. Derivation of reference signal from output of the follower, rather than directly from the oscillator (or output of amplifier 1), holds no particular advantage in analytical work, but is preferred for purposes of electrochemical kinetic studies as it eliminates possible error arising from phase shift (other than 180°) in amplifier C.

Phase-selective second-harmonic a.c.

polarograms shown in Figures 11 and 12 have the form of the second derivative of the d.c. polarogram, as expected. The ferric-ferrous system behaves nearly reversibly (18, 30) under conditions employed, yielding nearly symmetrical peaks for conventional and phase-selective second harmonic polarograms. The cadmium system shows small, but definite, deviations from ideality at 80 c.p.s. which become more apparent at higher frequencies (28),

indicating partial rate control by some step or steps in addition to diffusion. This result is not unexpected (3).

Reproducibility of phase-selective second-harmonic polarograms is observed to be within ± 0.5 to 0.7% relative standard deviation when conditions comparable to those used in Figures 11 and 12 are employed. Such polarograms have been obtained with input frequencies ranging from 10 to 1000 c.p.s. with the instrument described. The instrument has not been applied to phase-selective detection of harmonics beyond the second although this should be possible.

A. C. POLAROGRAPHIC PHASE ANGLE RECORDING

Considerable interest has attended measurement of a.c. polarographic phase angles for purposes of studying kinetics and mechanisms of electrode processes (3, 26, 27, 33, 34). To date, all reported techniques applicable to phase-angle measurement have involved point-by-point methods employing either an impedance bridge to determine resistive and capacitive components of cell impedance (17, 18, 33), an oscilloscope to measure phase angle and amplitude of total cell current (3), or, as in the approach evaluated above, oscilloscopic measurement of phase angles (point-by-point) combined with an a.c. polarograph providing automatic recording of current amplitudes (26, 27). The need to compensate for double-layer charging current contributions and series iR drop to obtain faradaic current parameters necessitates knowledge of either resistive and capacitive components of cell

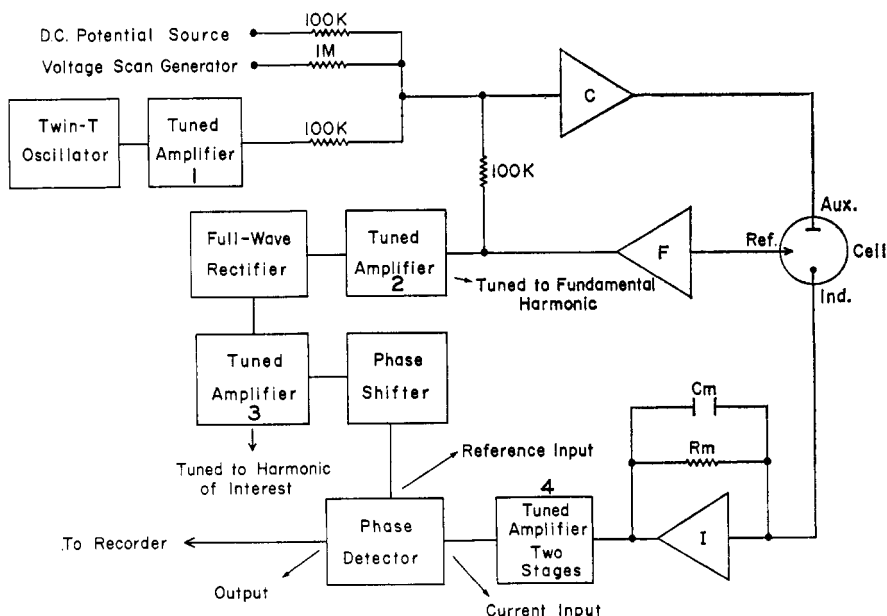


Figure 13. Schematic of instrument for phase-selective second-harmonic a.c. polarography

Adaptation of the instrument under consideration to phase angle recording is shown in Figure 14. The current and potential signals, after tuned amplification, are converted to square waves by high gain limiter (trigger) circuits. Square wave output of the trigger changes sign each time sine wave input crosses zero. Amplitude of the square wave is virtually in-

[illegible]

Amplification S—stabilized amplifier; K2-XA, K2-P combination

The full-wave rectifier employed in this work is basically an absolute-value circuit commonly used in analog computing (24), suitably modified for the present purpose. The circuit is given in Figure 16. A damping condenser, C_d , serves to filter out a.c. components of the rectified signal for purposes of recording. A bucking potential makes possible versatility in selection of phase-angle interval to be recorded—i.e., a phase angle of any magnitude can be made to correspond to a zero d.c. signal to recorder. The phase shifter also accomplishes the same end in that it allows adjustment of apparent phase angle between potential and current signals to any value. Two methods of interval selection are

Regarding use of the phase shifter, it is unnecessary that the phase angle between the two square waves be identical to the actual phase angle between alternating component of cell current and applied alternating potential because of the method of calibration

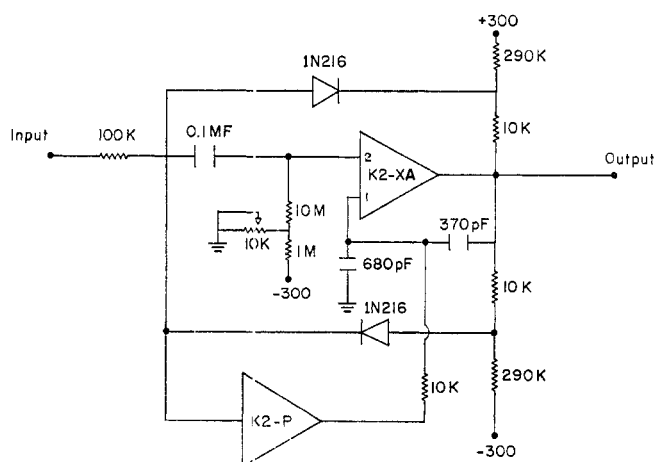


Figure 16. Full-wave rectifier

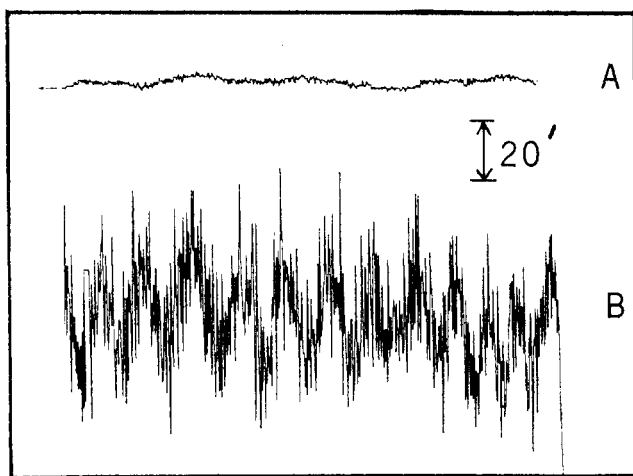


Figure 17. Phase-angle noise levels with instrument for phase-angle recording

Recorded with dummy cell: 1000 ohm impedance
Applied: 80 c.p.s., 10 mv. peak-to-peak
Recording time: 3.5 minutes

(A) With twin-T oscillator
(B) With commercial oscillator (freq. stability $\cong 0.4\%$)

employed. Calibration amounts to replacing the polarographic cell with a dummy cell consisting of a parallel or series RC circuit, synthesizing known phase shifts, and noting resulting recorder deflection. A calibration curve is thus obtained showing phase shift in electrolytic cell *vs.* recorder deflection. Calibration of a typical recording requires 1 to 2 minutes.

A typical phase-angle recording for a complete a.c. wave is given in Figure 18 showing phase angle between total cell current and alternating potential at end of drop life as a function of d.c. potential. The recording shows a wave similar in form to that observed in a normal a.c. polarogram (current-amplitude measurement). This is because deviations of phase angle from 90° are proportional to the magnitude of the faradaic contribution. While part of the resistive component of the cell impedance is due to ohmic potential drop, it is insufficient to account for small phase angles observed, indicating considerable nonideality of the Cd^{+2} system under these conditions in agreement with above second-harmonic results. Although linear response is anticipated, nonlinearity at low signal levels is observed because of diode imperfection and differences in square wave rise time. Comparisons of recorded phase angles and those obtained with the point-by-point method show excellent agreement.

By generating a second-harmonic reference signal, as done in phase-selective detection of second-harmonic currents (Figure 13), an instrument suitable for recording second-harmonic phase angles is obtained (see Figure 19). A typical recording is shown in Figure

20. It is characterized by a considerable difference in magnitude of the two waves and a very steep slope on the rising portion of the larger wave. The large difference in signal levels is anticipated because of very small nonfaradaic contributions and the 180° difference in phase angle between the two faradaic waves, corresponding to phase shift required to observe a change from zero signal to maximum signal. Thus, with proper instrument adjustment, zero signal may be obtained in the vicinity of one wave and maximum signal for the other. This is not observed in Figure 18 because of imperfect instrument adjustment, contributions by nonfaradaic components,

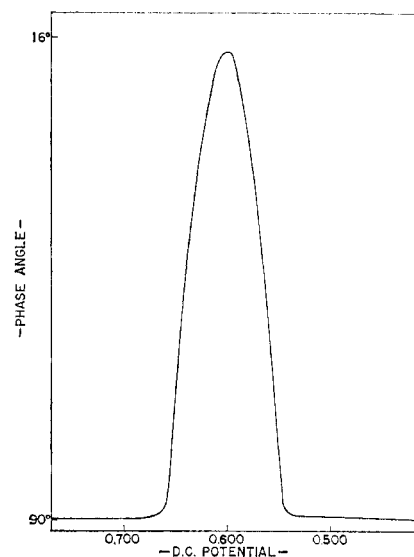


Figure 18. Fundamental-harmonic phase-angle recording

System: $3 \times 10^{-3}M$ $Cd(II)$, $1.0M$ Na_2SO_4
Applied: 160 c.p.s., 12 mv. peak-to-peak
Measured: phase angle between a.c. current (160 c.p.s.) and applied alternating potential

D.C. scan rate: 50 mv. per minute

and/or noise levels in the amplifier. Rapid increase in signal level at the beginning of the larger wave is observed because of independence of signal on current amplitude. The instrument is responding to sudden phase shift of almost 180° , not to gradual increase in amplitude. Nonfaradaic components and noise levels prevent the slope of this rapidly rising portion from being larger.

Utilization of a.c.-polarographic phase-angle recording to increase convenience and rapidity of data collection for basic electrochemical studies does not represent the only application. Some

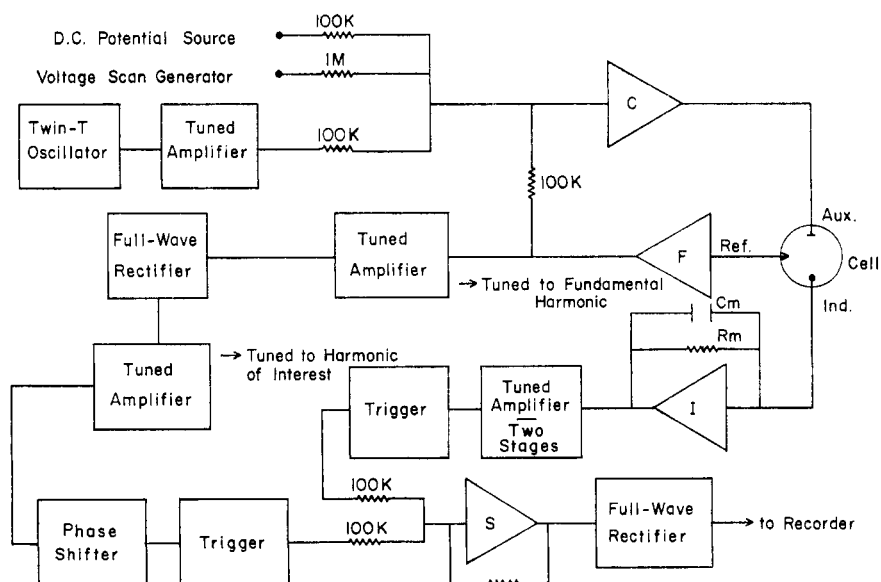


Figure 19. Schematic of instrument for second-harmonic phase-angle recording

simple considerations indicate potential advantage in the area of trace analysis. For example, consider the idealized system in which ohmic resistance in the cell and external circuitry may be neglected. The influence of a reversible faradaic process on phase angle of total fundamental-harmonic current may be calculated as follows. Defining double-layer charging current as

$$i_c = A_c \cos \omega t \quad (1)$$

then the faradaic component is given by

$$i_f = A_f \cos \omega t + A_f \sin \omega t = 2^{1/2} A_f \sin \left(\omega t + \frac{\pi}{4} \right) \quad (2)$$

(equal sine and cosine terms for a reversible system). The total fundamental harmonic current is

$$i_t = (A_f + A_c) \cos \omega t + A_f \sin \omega t = [(A_f + A_c)^2 + A_f^2]^{1/2} \times \sin \left(\omega t + \cot^{-1} \frac{A_f}{A_f + A_c} \right) \quad (3)$$

corresponding to a phase angle of

$$\theta = \cot^{-1} \frac{A_f}{A_f + A_c} \quad (4)$$

and a per cent faradaic component of

$$\% \text{ faradaic} = \frac{100 \sqrt{2} \cot \theta}{(1 + \cot^2 \theta)^{1/2}}$$

In a phase-angle recording designed for purposes of analysis, the instrument is adjusted to give zero output when

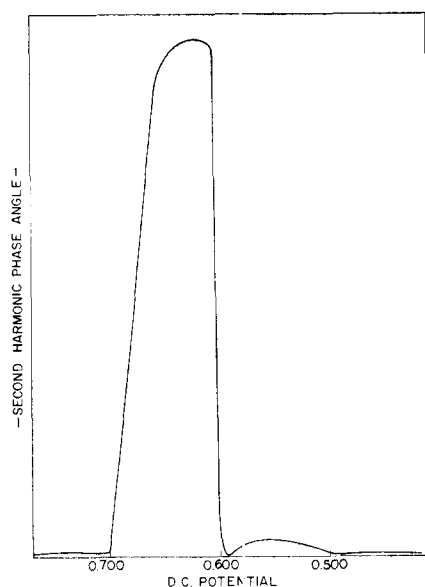


Figure 20. Second-harmonic phase-angle recording

System: $3 \times 10^{-3}M$ Cd (II), 1.0M Na_2SO_4
Applied: 160 c.p.s., 12 mv. peak-to-peak
Measured: Relative phase angle variation between second harmonic current (320 c.p.s.) and second harmonic reference signal generated from alternating potential. Ordinate uncalibrated
D.C. scan rate: 50 mv. per minute

$A_f = 0$ ($\theta = 90^\circ$ when ohmic potential drop may be neglected). Deviations of phase angle from 90° correspond to faradaic contributions. A 2° change in phase angle can be made to correspond to full-scale recorder deflection with the present instrument. A change in phase angle from 90° to 88° indicates that $\cot \theta$ varies from 0.000 to 0.035. Thus, a faradaic component comprising only 4.9% of total fundamental-harmonic current can yield a full-scale deflection in phase-angle recording. For a typical, reversible, 1-electron reduction this per cent faradaic current corresponds to a concentration of the order of $10^{-6}M$ at frequencies in the vicinity of 10 to 30 c.p.s. With present noise levels, the limit of detection would be approximately an order of magnitude lower for such a system. These considerations have neglected influence of ohmic potential drop in solution, electrodes, and external circuitry which, while greatly reduced by operational-amplifier circuitry, can still be the limiting factor at high sensitivities. The effect of iR drop is to make phase angles differ from 90° in absence of faradaic influence, this difference being dependent on d.c. potential and mercury drop life. However, with aqueous solutions and specially-designed capillaries (18), series resistance probably can be made 10 ohms or less. Combined with a typical double-layer capacity (1 $\mu f.$ at maximum drop size) this resistance would not alter seriously above conclusions regarding sensitivity at low frequencies. With stationary electrodes, it is believed that series resistances of less than an ohm can be obtained in aqueous solutions enabling full advantage to be taken of sensitivity inherent in phase-angle recording.

The basis of fundamental-harmonic phase-angle recording for purposes of trace analysis lies in the principle that resistive components of the a.c. polarographic current are attributable primarily to faradaic contributions. Thus, this technique cannot be considered different in principle or in performance expectations from phase-selective detection of fundamental harmonics. The only basis for choice between the techniques might lie in practical considerations (costs, etc.).

The above discussion regarding analytical sensitivity of fundamental-harmonic phase-angle recording can be applied analogously to second harmonics. For example, a second-harmonic faradaic component arising from a reversible process and consisting of only 4.9% of total second-harmonic current, potentially can be detected with ease by observing the phase angle change due to this component. Because of relatively very small contributions of nonfaradaic processes to second harmonics, such a situation would

correspond to concentrations well below the 10^{-6} to $10^{-7}M$ limit of detection anticipated for fundamental-harmonic measurement. Such high sensitivity is expected also for phase-selective detection of second-harmonic currents.

These conclusions regarding sensitivity of techniques under discussion are based solely on consideration of efficiency in discriminating against charging-current contributions. For work with very low concentrations, electronic noise levels become an important factor. Despite the use of tuned amplifiers, etc., noise levels in the present instrument would not allow realization of full potentialities of phase-selective second-harmonic a.c. polarography or second-harmonic phase-angle recording.

POSSIBLE IMPROVEMENTS ON PRESENT INSTRUMENTATION

Considerable improvement on the present instrument is suggested within the framework of the operational amplifier approach, much of which would be superfluous unless one is interested in high-sensitivity applications (higher harmonic measurements, trace analysis, etc.). Application of d.c. power, low noise solid-state instrumentation, higher-performance amplifiers, and more stable oscillators are among typical modifications which should effect improved performance. In addition, a unique method of detecting a.c. signals representing possible substantial improvement in instrument sensitivity and a unified approach to many a.c. polarographic techniques of interest has been suggested to us (5). The technique involves electronic multiplication of the a.c. signal to be analyzed by a sinusoidal signal of the same frequency and phase as the component to be detected. A d.c. component generated by this operation is measured. The principle behind this approach is recognized best by consideration of the trigonometric relations (6)

$$\sin^2 \omega t = \frac{1}{2}(1 - \cos 2\omega t) \quad (5)$$

$$\cos^2 \omega t = \frac{1}{2}(1 + \cos 2\omega t) \quad (6)$$

$$\sin \omega t \cos \omega t = \frac{1}{2} \sin 2\omega t \quad (7)$$

$$\sin \omega_1 t \sin \omega_2 t = \frac{1}{2} \cos(\omega_1 - \omega_2)t - \frac{1}{2} \cos(\omega_1 + \omega_2)t \quad (8)$$

$$\cos \omega_1 t \cos \omega_2 t = \frac{1}{2} \cos(\omega_1 - \omega_2)t + \frac{1}{2} \cos(\omega_1 + \omega_2)t \quad (9)$$

$$\sin \omega_1 t \cos \omega_2 t = \frac{1}{2} \sin(\omega_1 + \omega_2)t + \frac{1}{2} \sin(\omega_1 - \omega_2)t \quad (10)$$

It is seen that d.c. components are generated only by multiplication of two signals identical in frequency. Also, the d.c. component is proportional to the cosine of the phase angle between the two signals being multiplied. Thus, measurement of this d.c. component (low pass filtering of the output of the multiplier) effects frequency-selective and phase-selective detection of the a.c. signal. Frequency selectivity can be made sufficiently good that this approach represents an alternative to the use of tuned amplifiers (5). With the multiplication approach the resonant frequency of the instrument is determined by frequency of the multiplying signal. Because the cell alternating-current signal and the multiplying signal are derived from the same oscillator, resonant frequency is always identical to the frequency of the signal of interest. Thus, oscillator-frequency instability will represent little problem if multipliers are used as a means of detection.

Electronic multipliers based on the quarter-square method or pulse height-pulse width modulation (23) appear to have frequency response and accuracy sufficient for a.c. polarography at audio frequencies. Because operational amplifiers are usually an integral part of electronic multipliers, this approach represents another application of operational amplifiers to a.c. polarography.

ACKNOWLEDGMENT

The author is indebted to W. H. Reinmuth under whose guidance the basis for this work was established. Thanks are due to D. D. DeFord and

E. H. Nagel for many valuable suggestions and discussions.

LITERATURE CITED

- (1) Bauer, H. H., *J. Electroanal. Chem.*, **1**, 256 (1960).
- (2) Bauer, H. H., Elving, P. J., *ANAL. CHEM.* **30**, 341 (1958).
- (3) Bauer, H. H., Elving, P. J., *J. Am. Chem. Soc.* **82**, 2091 (1960).
- (4) Booman, G. L., *ANAL. CHEM.* **29**, 213 (1957).
- (5) Boonshaft and Fuchs, "High Performance Feedback Controls," Applications Bulletin 711A, Boonshaft and Fuchs, Inc., Hatboro, Pa., Jan. 1963.
- (6) Burington, R. S., "Handbook of Mathematical Tables and Formulas," p. 18, Handbook Publishers, Inc., Sandusky, Ohio, 1948.
- (7) Cakenberghe, J. van, *Bull. Soc. Chim. Belges* **60**, 3 (1951).
- (8) DeFord, D. D., Division of Analytical Chemistry, 133rd Meeting, ACS, San Francisco, Calif., April 1958.
- (9) DeFord, D. D., Nagel, E. H., Division of Analytical Chemistry, 144th Meeting, ACS, Los Angeles, Calif., April 1963.
- (10) Erbeling, W., Cooke, W. D., Division of Analytical Chemistry, 140th Meeting, ACS, Chicago, Ill., September 1961.
- (11) Jessop, G., British Patent No. 640,768 (1950).
- (12) Kelley, M. T., Fisher, D. J., Jones, H. C., *ANAL. CHEM.* **31**, 1475 (1959); **32**, 1262 (1960).
- (13) Kelley, M. T., Fisher, D. J., Jones, H. C., Division of Analytical Chemistry, 144th Meeting, ACS, Los Angeles, Calif., April, 1963.
- (14) Malmstadt, H. V., Enke, C. G., Toren, E. C., Jr., "Electronics for Scientists," pp. 241-2, W. A. Benjamin, Inc., New York, 1962.
- (15) Milner, G. W. C., "Principles and Applications of Polarography," pp. 132-3, Longmans, Green, New York, 1957.
- (16) Paynter, J., Reinmuth, W. H., *ANAL. CHEM.* **34**, 1335 (1962).
- (17) Randles, J. E. B., *Discussions Faraday Soc.* **1**, 11 (1947).
- (18) Randles, J. E. B., Somerton, K. W., *Trans. Faraday Soc.* **48**, 937, 951 (1952).
- (19) Reilley, C. N., *J. Chem. Ed.* **39**, A853, A933 (1962).
- (20) Reinmuth, W. H., Paynter, J., Smith, D. E., Columbia University, New York, N. Y., unpublished work, 1961.
- (21) Rogers, A. E., Connolly, T. W., "Analog Computation in Engineering Design," pp. 25-8, McGraw-Hill, New York, 1960.
- (22) *Ibid.*, p. 127.
- (23) *Ibid.*, p. 429.
- (24) *Ibid.*, p. 430.
- (25) Senda, M., Delahay, P., *J. Am. Chem. Soc.* **83**, 3763 (1961).
- (26) Smith, D. E., *ANAL. CHEM.* **35**, 610 (1963).
- (27) Smith, D. E., Division of Analytical Chemistry, 140th Meeting, ACS, Chicago, Ill., September, 1961; D. E. Smith, Ph.D. thesis, Columbia University, New York, 1961; D. E. Smith, W. H. Reinmuth, Columbia University, New York, N. Y., unpublished data, 1961.
- (28) Smith, D. E., Northwestern University, Evanston, Ill., unpublished work, 1963.
- (29) Smith, D. E., Reinmuth, W. H., *ANAL. CHEM.* **32**, 1892 (1960).
- (30) *Ibid.*, **33**, 482 (1961).
- (31) Tachi, I., Senda, M., *Bull. Chem. Soc. Japan* **28**, 632 (1955).
- (32) Takahashi, T., Niki, E., *Talanta* **1**, 245 (1958).
- (33) Tamamushi, R., Tanaka, N., *Z. Physik. Chem. N.F.* **21**, 89 (1959).
- (34) *Ibid.*, **28**, 158 (1961).
- (35) Underkoffler, W. L., Shain, I., *ANAL. CHEM.* **35**, 1778 (1963).
- (36) Walker, D. E., Adams, R. N., Alden, J. R., *Ibid.*, **33**, 308 (1961).
- (37) Woodbury, J. R., *Electronics* **34**, 56 (Sept. 1961).
- (38) Yu, Y. P., *Ibid.*, **31**, 99, Sept. (1958).

RECEIVED for review June 4, 1963.
Accepted August 12, 1963. Division of Analytical Chemistry, 144th Meeting, ACS, Los Angeles, April 1963. Work supported by the National Science Foundation.

A Practical Instrument Synthesizer

CHARLES F. MORRISON¹

Department of Chemistry, Washington State University, Pullman, Wash.

► Construction details are presented for the Generalized Analog Instrument Synthesizer Model II (GAIS II). Over 40 analytical techniques have been tested with this Instrument Synthesizer serving as the electronics for each. Through use of a special manifold, GAIS II makes available the versatility of the operational amplifier in a manner convenient for laboratory use. The manifold is programmed with plug-in resistors, capacitors, diodes, etc. to be the required instrument functions. The amplifiers are then interconnected with a mounted collection of instrument hardware to become the electronics for a given application. In addition to general laboratory service, GAIS II has served as a

design prototype for specific instruments. It has taken the place of much of the equipment used for courses in instrumental analysis and chemical instrumentation. A bimodal, potentiometric, automatic titrator, and a recording, linear conductance bridge are presented as examples of instruments synthesized by this device.

MANY SPECIFIC USES of operational amplifiers in analytical instruments have been reported and the virtues of this unique type of instrumentation have been extolled before our professional societies.

The circuitry which performs the basic logical and mathematical opera-

tions in analog computing is obviously capable of replacing much specific chemical-instrument circuitry. It seems logical then that an analog computer might serve as a very versatile instrument synthesizer. It could be programmed to be the desired electrical and electronic functions for whatever instrument was desired. Ewing and Brayden (2) have performed tests on the Heathkit computer as a laboratory instrument, and several multipurpose analog devices have been reported (6, 7, 14). The commercially available analog computer manifolds were not sufficiently flexible for our anticipated

¹ Present address, Granville-Phillips Co., Box 1290, Boulder, Colo.