Fast-writing Precision Apparatus for Continuous Recording of Electrolytic Resistance

CARL-OVE ANDERSSON and EINAR STENHAGEN

Department of Medical Biochemistry, Institute of Medical Chemistry, University of Uppsala, Sweden

OLOF MELLANDER

Department of Medical Biochemistry, University of Gothenburg, Sweden

A high precision apparatus is described for the continuous recording of resistance. Full-scale response in less than 5 seconds is obtained for resistance-changes within a range variable at will from 2 to 1 900 ohms. The noise-level of the apparatus in its present form is equivalent to resistance-changes of about $1 \times 10^{-4}$ at a cell-resistance of 500 ohms. In practice, sensitivities up to $1 \times 10^{-4}$ may be employed without noise or zero drift in the recordings, provided that resistance-changes due to temperature-drift are eliminated.

During the course of a chemical reaction involving ions and taking place in aqueous solution, some of the ions originally present disappear and new ones are formed, causing change in the electrolytic conductivity of the solution. Analytical procedures involving conductometric titrations are based upon the fact that the slope of the curve conductivity-added reagent shows an abrupt change in direction at the equivalence point. Similar changes are noted when the state of aggregation of the solute is changed. Measurements of conductivity are therefore useful in following micelle formation in solutions of paraffin-chain salts and bile salts.

Reactions in biological systems such as enzymatic hydrolysis may also be traced by measurement of the conductivity of the solutions. With the methods ordinarily used for following enzymatic hydrolysis it is impossible to cover the initial part of the reaction. In most methods samples are taken after different time-intervals, and the information obtained is thus limited to a series of

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discrete points on the reaction-time curve. The means of stopping the enzymatic reaction in the samples after they have been removed from the system are frequently such that they might influence the analytical results through secondary reactions. In contrast to this, measurement of the conductivity often enables reactions to be followed without interference but, as the ionic strength of the system is usually high and the often rapid reaction produces only small changes in the conductivity of the solution, a fast, sensitive recording system is necessary.

In recent years a number of devices have been described for recording the electrolytic conductivity of the effluent from chromatographic columns. In this particular connexion a high recording-speed is not necessary, and none of the devices described appears to possess the combination of speed, accuracy, and stability needed for following chemical reactions of various types.

The conversion of a Sheldovsky precision bridge into a fast-writing resistance recorder is described below. A block diagram of the apparatus is shown in Fig. 1.

The bridge is fed from a 1000 c/s oscillator. The detector signal is amplified by a three-stage amplifier with automatic gain control, which prevents overloading of the recording system in case of considerable unbalance. The amplified signal and a reference signal from the oscillator are applied to a phase-sensitive detector. After filtering, the output of the phase-sensitive detector is fed via a cathode-follower stage to the input of the amplifier of a Speedomax-G recorder. To the potentiometer shaft of this recorder a linear high-precision potentiometer is mechanically coupled (P in Fig. 1), which forms parts of two arms of the bridge (cf. Fig. 2), the moving contact being connected to one side of the input of the detector amplifier. A signal from the bridge

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makes the recorder pen move until balance has been restored through the potentiometer attached to the recorder shaft. In order to prevent hunting of the servo system an adjustable amount of velocity feed-back to the recorder amplifier is introduced via a mixer from a tachometer generator geared to the balance motor of the recorder.

The use of a detector amplifier with automatic gain control ("compression amplifier"), variable phase-control in the phase-sensitive detector, velocity feed-back in the servo system, and an electro-mechanical filter in the form of a motor-generator between the A.C. mains and the power supply units of the apparatus, has resulted in very satisfactory sensitivity, stability, and speed of response.

The theory of the alternating-current Wheatstone bridge is found in standard texts. The theoretical aspects of bridges for measuring electrolytic conductivity, and the sources of error involved in such measurements, have been discussed by Jones and Josephs and by Shedlovsky. A precision conductivity-bridge assembly has also been described by Luder. A new type of alternating-current bridge suitable for measuring electrolytic resistance has recently been described by Easton and Lamson.

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DESCRIPTION OF APPARATUS

Wheatstone bridge. The Shedlovsky type bridge 7 is similar to that used by Mellander and Stenhagen 12. A shunted 1 000-ohm precision potentiometer P (Fernsteuergeräte PW 70 *), mechanically coupled to the potentiometer shaft of the recorder, is electrically connected between the decade and the conductometric cell as shown in Fig. 2. The movable contact is connected to one side of the primary of the detector input transformer. By means of the variable shunt, R1, the resistance range covered by full-scale travel of the recorder pen can be continuously adjusted from about 2 ohms to 1 900 ohms. Alternatively, a series of fixed shunts is provided for selecting standard resistance ranges of 20, 50, 100, 200, 500, and 1 000 ohms.

In order to determine the initial resistance of the cell, the shunt R1 is shorted, and a pair of headphones connected through a jack to the output side of the detector amplifier. The headphones are also necessary during the initial adjustment of the phase-sensitive detector.

The potentiometer, P, (Fig. 2) has 1 200 turns for 1 000 ohms. The resultant limit of precision is thus, for a recorder scale-range of 1 000 ohms, of the order of 1 ohm (0.1 %), i.e. the same as the pen-setting precision of the recorder. On lower scale-ranges the limitation of the precision due to the limited number of turns of the potentiometer is therefore negligible. Early in the development of the apparatus a 100-ohm potentiometer was used, when the recorder could be made to count the number of turns of the winding. The figure obtained in this way agreed with that given by the manufacturer.

All fixed resistors are of manganin wire ** (Ayrton-Perry winding or, for resistances above 200 ohms, single layer on mica card). The values of the fixed resistors R2—R6 must be determined experimentally. The bridge is fed from an oscillator via a shielded transformer (Svenska Radiobolaget XLT 504), the voltage across the secondary of which is usually adjusted to one volt. The requirements for low content of harmonics in the output of the oscillator do not seem critical. Both a simple, home-made RC oscillator and a commercial instrument (Philips GM 2307) have been used.

Detector amplifier. The circuit diagram of the detector amplifier is shown in Fig. 3a. Three resistance-capacity coupled stages using two 6SK7 and one 6V6 tubes give a maximum voltage amplification of 70 000 for an input voltage of 10 microvolts. The noise-level of the amplifier at the maximum gain was found to be equivalent to 10 microvolts at the primary of the input transformer. As the input voltage increases in amplitude the gain is reduced by the automatic volume control through the 6H6 diode. At 0.1 mV input at 1 000 cycles/sec the gain is 50 000; at 100 mV input it has been reduced to 600 times. The time constant of the automatic gain-control is about 2 seconds, and the amplifier can handle input signals of up to 0.3 volts without appreciable distortion. The low gain at low frequencies reduces noise due to 50-cycle pick-up. The shielded input transformer Tr has a turns-ratio of 1:6 (Svenska Radio-

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* Obtainable from AB Impuls, Stockholm.
** Made by Svenska Mätapparater Fabriks AB, Enskede.
Fig. 3. a) Detector amplifier and b) phase-sensitive detector circuits.

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bolaget type XLT 505). The position and orientation of this transformer have not proved critical.

Phase-sensitive detector. The circuit (Fig. 3) is almost identical with that used by Kinell, who also discusses the theory. (For a general discussion of phase-sensitive detectors see Ahrendt.) A small galvanometer with a sensitivity of 2 micro-amperes per scale division (Siemens, 450 ohms internal resistance) indicates the sign and magnitude of the direct-current output of the cathode follower which is fed to the input terminals of the recorder amplifier.

RECORER AND ARRANGEMENT OF VELOCITY FEED BACK

A Leeds and Northrup Speedomax-G recorder with a pen travel time of 4.5 seconds across the chart is used. As shown in Fig. 4, a small direct-current generator (Pullin 5V/4798 *) is geared directly to the pen-driving motor of the recorder via a pair of 1:1 helical gears for crossed axles (Kremp und Söhne, Wetzlar, Germany). There must be no backlash in these gears. To prevent hunting of the servo system, part of the output of the generator is fed back to the input of the recorder amplifier via a mixer (Fig. 1) consisting of a 200-ohm potentiometer connected in series with one of the recorder-amplifier input leads. One of the generator terminals is connected to the movable contact,

* Obtained through Ingeniörsfirma Hugo Tillquist, Stockholm.
Fig. 5. Anode-voltage power supply.

Fig. 6. Filament power supply.

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and the other to one end of the potentiometer-winding. By adjusting the potentiometer the desired amount of feed-back can be introduced.

**Power-supply.** The stabilized anode current supply and the stabilized direct-current filament supply used are identical with those described by Kinell. For convenience the circuit diagrams are reproduced in Figs. 5 and 6.

When first testing the completed apparatus in the laboratory the recordings were very disturbed by irregular 'spikes'. These were evidently caused by disturbances and transients in the 220-volt A.C. mains, as they disappeared completely when the apparatus was connected to a separate 220-volts alternating-current generator driven by a motor connected to the A.C. mains.

**PERFORMANCE OF THE APPARATUS**

Fig. 7 shows the response of the recorder for step-wise resistance-changes of 10 ohms each on the 100 ohm recorder range for cell-resistance of the order of 1,000 ohms. The pen-positions are reproduced within one pen-line width, i.e. the pen-setting precision of the recorder. The feed-back was adjusted to give a slight overshoot for the step-wise resistance change. Between the steps the paper chart was moved forwards by hand. There is complete freedom from noise.

Fig. 8 shows the response to step-wise resistance changes of 100 ohms with the paper travelling at a speed of 14" per hour (5.9 mm per minute).

The performance of the apparatus at high sensitivity is illustrated in Fig. 9, which shows the response of the recorder to resistance changes in steps of 1, 0.1, and 0.05 ohms, respectively, at a total resistance (decade box) of 5,000 ohms and a recorder-range of 6 ohms. The steps of 0.05 ohms correspond to a sensitivity of 1 part per 100,000. Taking into account variable contact resistance in the decade switches it appears that the reproducibility of the apparatus is of the order of 1:200,000, or 0.0005 per cent.

At these high sensitivities the galvanometer across the output of the phase-sensitive detector showed rapid fluctuations equivalent to resistance-changes of 0.005 ohms (1:10⁴), which may be taken as representing the noise-level of the system. Superimposed upon these small rapid fluctuations were slower

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**Fig. 7.** Recording of step-wise resistance changes of 10 ohms at a recorder range of 100 ohms. Paper moved forward by hand between steps.

**Fig. 8.** Recording of step-wise resistance changes of 100 ohms at a recorder range of 200 ohms. Paper speed 5.9 mm per minute.

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Fig. 9. Recordings of small changes in resistance at a total 'cell' resistance of 5000 ohms and a recorder-range of 6 ohms. From above downwards: 2 steps of 0.05 ohm; 3 steps of 1 ohm; and 10 steps of 0.1 ohm. Paper speed 5.9 mm per minute.

oscillations equivalent to resistance-changes of about 0.01 ohms. These were found to be caused by small variations in the voltage of the motor generator. It seems likely that a fly-wheel on the shaft of the motor generator or the use of a larger machine * would eliminate this type of noise.

Effect of capacitative unbalance. For a cell-resistance of 500 ohms a capacitative unbalance of 400 pF introduced a zero drift of less than 0.25 ohm, or 0.05 %. The effect on the accuracy and speed of response was negligible. For a cell-resistance of 5000 ohms the zero drift was more pronounced, and the effect on the accuracy and speed of response became marked at unbalances of about 100 pF. Under the conditions of measurement the zero drift was more marked when the capacitance was decreased, the drift for —350 pF amounting to 21.5 ohms, or about 0.4 %.

It is obvious that the ideal instrument for recording changes in electrolytic resistance should also be capable of continuously correcting errors in the capacitative balance of the bridge, as a change in resistance is usually accompanied by a change in capacitance. Drake 5 has performed some measurements on a conductivity cell using the same voltage across the cell at different conductivities of the solution (electrolyte not specified). He found that the change in capacitance was a linear function of 1/R. From this he inferred that the capacitance of the electrolytic cell is proportional to the current density. If this were true, capacitative unbalance could be corrected by altering the voltage across the bridge. It is found experimentally, however, that an increase in the current density due to an increase in the voltage across the cell has practically no effect on the effective capacitance of the cell. Both the capacitance of the cell and the current density at constant voltage are approximately proportional to the concentration of the electrolyte, but there is no direct connexion between the two.

* The machine used had a capacity of 1.8 kW.

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During a run any capacitative unbalance developing may be traced on an oscilloscope connected across the output of the bridge amplifier. If the error becomes too large it may be corrected by manual adjustment. The simplest way to perform this correction automatically seems to be to arrange a separate servo system or recorder to make the adjustment at predetermined intervals as a standardizing operation. By reversal of these functions the instrument can of course be made to record capacitance changes in conducting systems. Such an instrument is being constructed.

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