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Automatic Recording of Conductance Titrations

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Conductivity titrations are customarily carried out by the tedious process of balancing a Wheatstone bridge after each addition of titrant, followed by manual plotting of points. The off-balance bridge system, suggested by Ewing (1956) and regularly used with thermal conductivity detectors for gas chromatography, can be used for solution conductivity measurements provided that alternating current is supplied to the electrodes and the bridge signal is rectified and then recorded.

The potentiometer \(R_r\) is helpful in attenuating the signal to fit the span of the 10 millivolt recorder. A 1.5 volt dry cell, \(B_1\) provides a bucking voltage, adjustable by \(R_v\), to help bring the recorder to the null position.

Electrodes were constructed by sealing 22 gauge platinum wire in the ends of two-inch lengths of 6 mm glass tubing, with about 2 cm of the exposed end bent into a flat coil. These electrodes were mounted about 2 cm apart in rubber stoppers fitted into a plexiglas support. Electrical contact is made by wires inserted into mercury in the electrode tubes.

At the start of a titration, \(R_b\) should be adjusted until the bridge is just slightly out of balance in the direction it will go after addition of the first portion of titrant. This setting avoids the sensitivity decrease near the balance point and also avoids confusion about whether any increasing signal is resulting from an increase or a decrease in resistance of the cell solution. It is convenient to place a small variable resistor, \(R_5\), in series with the bridge as indicated in the circuit diagram.

The circuit shown in Figure 1 is easily constructed and will produce satisfactory conductometric curves quickly and automatically. In this circuit \(R_1\) and \(R_2\) are 1500 ohm fixed resistors. An ordinary 5000 ohm potentiometer will serve for \(R_5\), but it is convenient to use a decade box since this affords a more accurate setting of the bridge balance as well as allowing the resistance of the cell to be read directly. Working voltage is supplied to the bridge by an audio oscillator, AO, set in the range of 2-4 KHz. The amplitude is adjusted so that the bridge output at balance is as close to null on the recorder as possible, with some intermediate position usually giving the minimum signal. The variable capacitor \(C_1\) may be used occasionally to bring the bridge to closer balance.

![Circuit for recording off-balance bridge signal](image)

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Figure 1. Circuit for recording off-balance bridge signal.

Figure 2. Conductometric titration of 16 ml of 0.003 N HCl with 0.01 N NaOH.
$R$, in series with the cell. This may be increased momentarily from zero during a titration and the resulting bridge unbalance will appear as a spike which will indicate increasing cell resistance.

Figure 2 shows a typical titration curve, using an inexpensive motor driven syringe for addition of the titrant. Endpoint precision naturally decreases with decreasing concentration of inert electrolyte. Sharp peaks are still obtained at a concentration of NaCl seven times that of the acid, but greater amplification of the signal is required, with consequent increase in noise.

The same circuit can be used for thermometric titrations, replacing the platinum electrode with a small 2000 ohm glass-coated thermistor.

**LITERATURE CITED**