

Apparatus for Precise Automatic Recording of Electrocapillary Curves.

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specimen and work out bubbles. The epoxy binds the ring mountings to the plate in a very convenient form for grinding, polishing, cleaning, etc., after which the individual mountings are pried off the plate for analysis.

For larger specimens, or for a wider selection of particles and structures than is provided by 1/4-inch mountings, a sheet of mylar (which serves as a parting layer) is taped flat onto a microscope slide and covered with double adhesive tape. Particles are sprinkled onto the tape and pressed slightly into the adhesive. Individual particles of interest can be placed in desired positions and orientations. Conductive epoxy is "puddled" over the particles. The adhesive prevents particles from being swallowed up and randomly distributed in the epoxy. Mylar and tape are stripped from the hardened mounting which is then ground to the desired

depth for analysis of particle cross sections.

Some materials are difficult to wet with epoxy, leaving undesirable voids and bubbles. Vacuum-desiccation of the sample particles prior to mounting improves their epoxy wettability and greatly reduces the formation of voids.

Vacuum Imbedding. In mounting detergent materials for cross-section analyses, some voids occur, even with previously desiccated particles, because of air entrapment by the irregular shaped granules. The following technique produces completely void-free mountings with improved physical stability. Previously desiccated granules are placed on double adhesive tape as for the "puddling" technique, but in the bottom of a square, transparent plastic box. The hinged box lid is set at an angle as shown in Figure 1, and a "retaining wall" built up with tape.

The lid is filled with epoxy-hardener mixture, and the entire assembly placed in a vacuum chamber. After a short evacuation, the volatility of the hardener causes the epoxy to foam up and flow over the sample particles, filling the entire volume of box and retaining wall. Readmission of atmospheric pressure then collapses the foam over the sample, closing voids and forcing the resin into all accessible pores and crevices in the granules.

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Apparatus for Precise Automatic Recording of Electrocapillary Curves

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MEASUREMENT of electrocapillary curves using a dropping mercury electrode (D.M.E.) is a familiar operation in polarographic and other electrochemical studies. These curves are useful in studying adsorption and the electrical double layer, as well as being applicable to the analysis of dilute solutions of surface active substances (1). Previous studies [(1, 2) and references contained therein] have indicated that under proper conditions surface tension values based on drop time measurements correspond very closely to those obtained from drop weight and Lippmann electrometer measurements. The determination of the drop time at many different potentials is a tedious task however, and several suggestions for automatic determination of this quantity have been made.

Ri'ha proposed a method based on the photoelectric measurement of the drop time and photographic recording of the electrocapillary curve employing a mirror galvanometer (5). Instrumentation for photoelectric measurement and digital presentation of drop times was described by Corbusier and Gierst (1), as well as manual plotting of the curve, was still required. This communication describes an apparatus based on principles similar to those of Corbusier

and Gierst, but using commercially available apparatus and allowing automatic digital and analog recording of the electrocapillary curve.

EXPERIMENTAL

A block diagram of the apparatus is shown in Figure 1. The light beam of a small bulb is interrupted by the fall of the mercury drop. This causes a momentary drop in the output current of the silicon photovoltaic light sensor, a Texas Instruments LS-222 sensor.

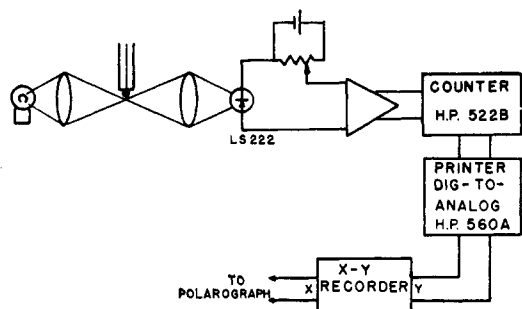


Figure 1. Apparatus for automatic electrocapillary curve measurements

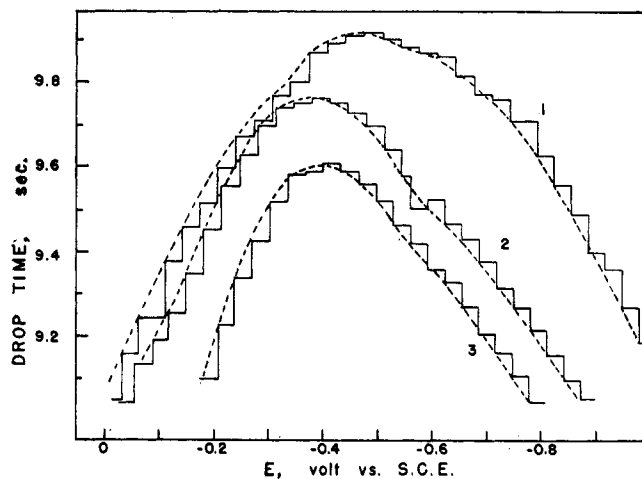


Figure 2. Typical results obtained with apparatus

Solution contained 1M potassium nitrate and
 1. Tetrabutylammonium iodide concentration, 0
 2. 0.042 mM
 3. 0.083 mM

The voltage pulse is brought to zero d.c. level and amplified with a d.c. amplifier (e.g., Heath EUW-19). The resulting pulse is used to trigger on a Hewlett-Packard 522B Electronic Counter. The next drop produces a pulse which stops the counter and causes the drop time to be printed on a Hewlett-Packard 560A digital recorder which also produces an analog voltage output to an X-Y recorder. In recording an electrocapillary curve the potential between the D.M.E. and the reference electrode is scanned with a polarograph and the drop time of every other drop is measured and recorded.

RESULTS AND DISCUSSION

Typical experimental curves are shown in Figure 2. The drop time is easily measured to the nearest millisecond; the precision and accuracy of the measurement is primarily governed by the stability and reproducibility of the D.M.E. capillary. In this work the capillary was fused to the standtube

and maintained in a fixed position while the cell was removed and replaced. Some precautions and suggestions for use of a D.M.E. capillary in drop time measurements is given by Corbusier and Gierst (1).

With the cells and solutions used in this study the action of the pulse alone was sufficient to cause triggering of the counter. Under some conditions the use of a multivibrator or flip-flop circuit following the amplifier results in more positive triggering action and may prove useful. Under some circumstances the triggering pulse could be generated by the abrupt variation in the capacitive current occurring at the fall of each drop (3, 4), but, as Corbusier and Gierst point out, this variation "may be poorly defined in the neighborhood of the potential of zero charge, especially in the presence of surface active agents which are adsorbed and considerably reduce the double layer capacity of the electrode." The output from the counter

can also be used to produce digital outputs on punched cards or paper tape which can be processed on a digital computer. Digital computer programs can be written for converting the drop time measurements to surface tensions, smoothing the data, and calculating the charge on the electrode, q , and the double layer capacity, C_{dl} , as a function of potential.

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Electrical Compensation for Nonzero Intercepts in Calibration Curves

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RECENTLY we have been concerned with automatic analyses based upon reaction rate measurements. An objective is to provide numerical readout of rate data calibrated in units of concentration of sought-for constituent. Frequently the linear relationship obtained between rate data and concentration has a nonzero intercept. To obtain direct readout in concentration units, it is necessary to compensate for these finite intercepts.

This problem is not unique to reaction rate methods. Park has discussed the problem as it applies to the titration blank (1). He has pointed out that if two or more samples of different weights are run under the same conditions, the amount of excess reagent will be the same in each case. Simple algebraic equations can be used to calculate the blank. In the work reported here a simple system has been developed for solving these equations electrically. It is assumed that quantitative data appear as a voltage of the form represented in Equation 1.

$$e = kX + e_z \quad (1)$$

where e is the output voltage, k is a constant representing the slope of the curve, X is the concentration of sought-for constituent and e_z is the zero intercept voltage. The output voltages e_1

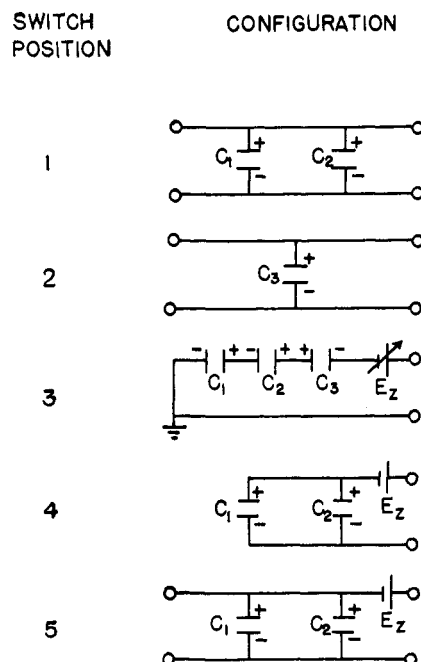


Figure 1. Functional representation of switching circuit

- Position 1. Store charge for concentration 1
 Position 2. Store charge for concentration 2 = 2 × concentration 1
 Position 3. Adjust E_z until output is zero
 Position 4. Calibrate output to read numerical value of concentration 1
 Position 5. Measure unknown concentrations

and e_2 at two different concentrations X_1 and X_2 are stored on capacitors and compared algebraically. In the special case when $X_2 = 2X_1$, the difference between twice e_1 and e_2 gives the zero voltage e_z as represented in Equation 2.

$$2e_1 - e_2 = e_z \quad (2)$$

A zeroing voltage which compensates for this difference compensates for the blank.

The system used and the mode of operation is represented in Figure 1. Position 1 permits the storage of e_1 on capacitors C_1 and C_2 . Position 2 permits storage of e_2 on capacitor C_3 . Position 3 permits the zeroing voltage E_z to compensate for the difference between $2e_1$ and e_2 which is e_z . Position 4 presents e_1 with zero correction and permits the output to be calibrated as an integral (1, 10 etc.) multiple of X_1 . Position 5 permits numerical values of unknown concentrations to be read directly.

Figure 2 shows details of the switching circuit required for the various functions represented in Figure 1. Capacitors used were Good-All, 2 μ f., 200 VDC (type 663 UW) paper mylar capacitors. The 100 K resistors are included to reduce the effects of switching transients. The Heath Operational Amplifier System (Heath Company, Benton