Optical drop fall detector for use with a dropping mercury electrode

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cell holder has four windows for maximum versatility. However, one could easily construct a holder with only two or three windows which would provide more thermal contact.

To use the holder for temperatures higher than 35 °C, it would probably be necessary to insulate the corner blocks. At higher temperatures, it might also be advantageous to use a metal with a higher heat capacity such as brass in place of aluminum. The minimum volume occupied by the cell holder is limited by the tubing. As constructed, it will fit into a sample compartment with dimensions of 3 cm × 8.5 cm × 7.5 cm. Additional room (about 10 cm × 10 cm × 10 cm) is needed if a bottom stirrer is used. For situations in which very precise temperature control or long term temperature stability is critical, continual temperature monitoring may be desirable.

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Optical Drop Fall Detector for Use with a Dropping Mercury Electrode

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In polarographic experiments where the time of the drop detachment from a dropping mercury electrode must be known, natural drop fall is frequently preferred to forcing the drop fall by mechanical means. Even when drop-knockers are used, drop fall detectors are often used to confirm that the drop fall actually occurred and that the natural period is not shorter than the mechanical one. Several different methods for the detection of natural drop fall have been reported. The natural voltage change that occurs at drop fall has been used (*1*); however, to detect this signal, the polarograph must be disconnected from the cell before drop fall by a switch or relay. The change in the ac impedance of the electrode has been used to detect the drop fall (*2–7*). This method requires an electronic connection to the electrode and the imposition of an ac signal on the electrode. The falling mercury drop has been used to interrupt a light beam to provide the drop fall signal (*8–11*). Although this technique has the advantage of requiring no electrical connection with the cell, the capillary must be very carefully aligned so that the falling drop will interrupt the light beam. An optical drop fall detector in which the optical alignment is less critical has been made by shining the light down the capillary and using a light pipe positioned at the end of the capillary to transmit light reflected by the mercury drop to an optical sensor (*12*).

We have also developed a "reflecting type" optical drop fall detector which maintains the advantage of having no electrical interaction with the cell; yet it requires no critical optical alignment and no probes within the cell. This drop fall detector monitors the amount of light reflected by the drop as it grows. When the drop detaches from the electrode, the amount of light reflected by the drop falls to zero. This sudden change in light level is used to produce the drop fall signal. The detector has two basic parts: an optical system to monitor the reflected light from the drop and an electronic monitor to measure the light and produce the drop fall signal.

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EXPERIMENTAL

Apparatus. The optical system is shown in Figure 1. The drop is illuminated from the side by a prefocused "penlight" lamp mounted outside of the cell. The lamp's position is adjusted to provide a maximum amount of light at the tip of the capillary. A piece of tape can be placed on the side of the cell to reduce stray reflections from the pool of mercury that eventually accumulates at the bottom of the cell. Part of the light which is reflected up the capillary by the mercury drop is diverted out of the capillary by a fiber optic light guide. For maximum light pick-up, the fiber optics are mounted in a notch ground into the side of the capillary above the top of the cell. The protective outer tubing was removed from the end of the pipe to permit greater flexibility in aligning the fibers, and the end of the fiber bundle was polished to reduce reflections and stray light pick up. Optical contact was further improved by using a clear epoxy cement to secure the fiber bundle in the notch. The fiber optic light guide can be of any convenient length and material. We used a 64-fiber 10-mil plastic fiber optic light guide (available from Edmund Scientific Co., Barrington, N.J. 08007, and others). The other end of the

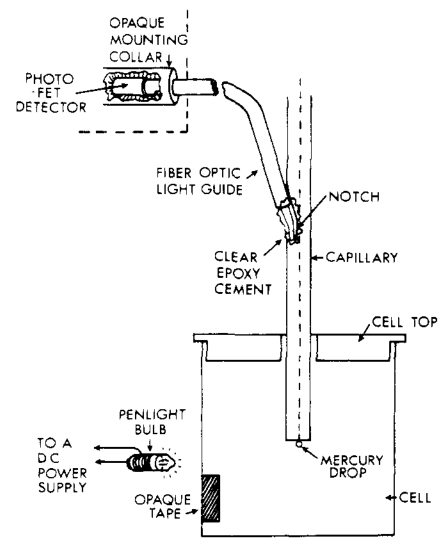

Figure 1. Optical arrangement of the drop fall detector

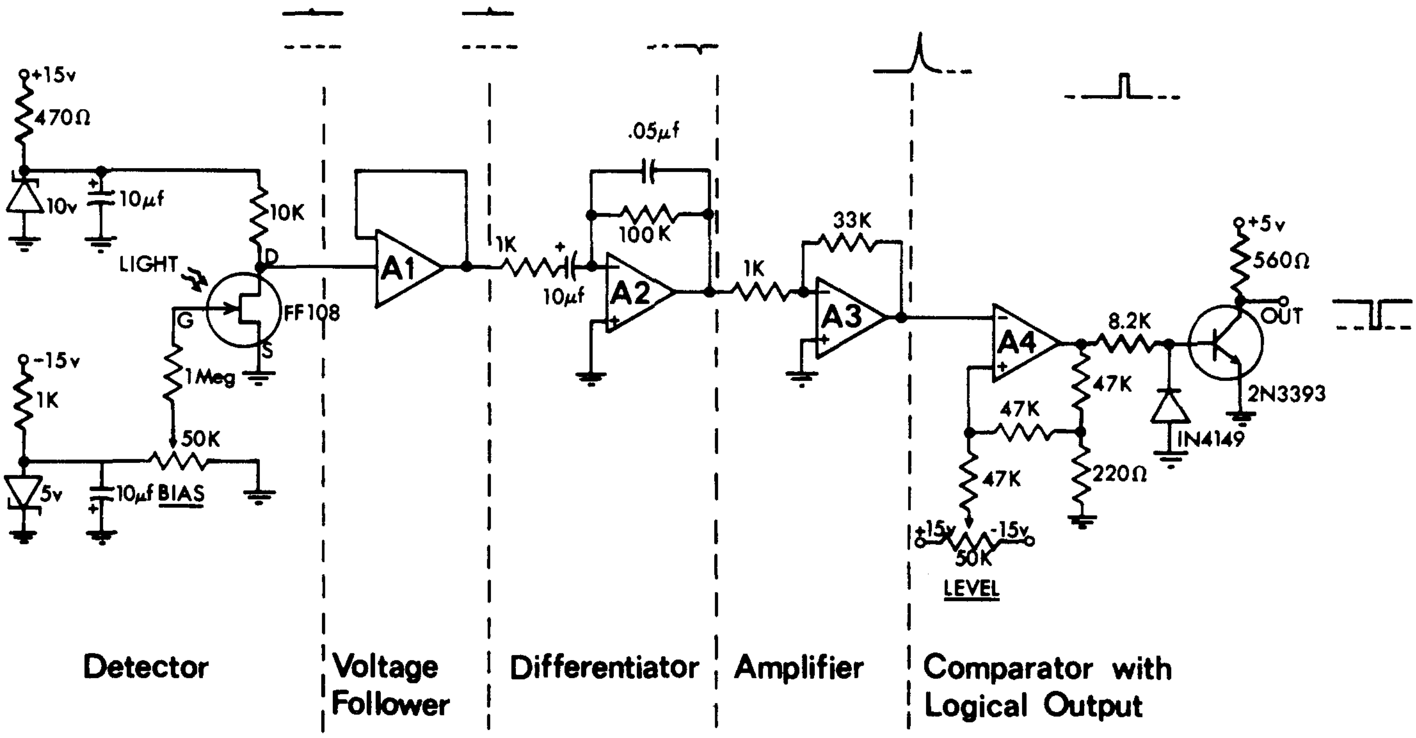

Figure 2. Circuit diagram of the monitor with typical waveforms

All amplifiers are 741 integrated circuits. All resistors are ¼ watt, 10%. Photo-FET is a type FF108 available from Teledyne Crystalonics, Cambridge, Mass. 02140

fiber optic guide was polished and firmly mounted in front of the photo-FET in the monitor module.

The drop fall monitor (Figure 2) measures the light from the fiber optic input and takes the first derivative of the light level. The photo-FET light detector is powered by two zener diode voltage supplies to reduce power supply fluctuation. The bias voltage applied to the gate of the FET (through the 1-megohm resistor) is adjusted with the bias potentiometer to give maximum detector sensitivity. In our monitors, the optimum sensitivity occurs when the output of the photo-FET is about 3.5 volts. The voltage follower is used to buffer the output of the photo-FET so that the differentiation stage will not affect the operation of the FET. The buffered output is then differentiated by an operational amplifier differentiator (A2) and amplified by the inverting amplifier (A3). This amplifies the signal change due to drop fall to a level where it can be easily and reliably detected by a comparator. The comparator compares the amplified output of the differentiator with the voltage from the trigger level potentiometer. The trigger level is adjusted to a level just below the peak voltage produced at drop fall. When the drop fall occurs, the input voltage to the comparator exceeds the reference voltage and the output of the comparator changes polarity, providing the output pulse. Hysteresis is introduced into the comparator through the resistor feedback network to reduce the possibility of multiple comparator triggering from the noise on the input signal. The output transistor converts the comparator output to a logic level signal that can be used to synchronize the polarographic instrumentation with the drop fall. The entire circuit for the monitor can easily be fitted inside a small box and mounted near the electrochemical cell.

NOTES ON OPERATION

To align the drop fall detector, aim the light from the lamp at the tip of the capillary where the drop is forming and then adjust the comparator trigger level potentiometer until a short pulse is observed at the time of the drop fall. Since the drop reflects light from sources other than the lamp, best results are obtained if the cell is at least partially screened from these sources. For example, if the ambient room light is provided by fluorescent tubes, a large 120-Hz signal will be present in the detector, producing an excessive uncertainty in the drop fall time and inducing multiple triggering of the detector output. The cell can be sufficiently shielded by a loose shroud of opaque cloth covering the cell.

The performance of the drop fall detector was tested in solvents with refractive indices ranging from 1.333 (water) to 1.507 (pyridine). If only a few centimeters of the capillary are immersed in the solution, the refractive index has little effect on the detector performance. The detector was also tested with colored and turbid solutions. In general, it was found that if the mercury drop can be seen through the cell solution under normal room lighting, then the drop fall detector can easily detect the drop fall. The detector performance with colored, turbid, or high refractive index solutions can be improved by enclosing the monitor circuit in a grounded metal case to reduce the background noise level.

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