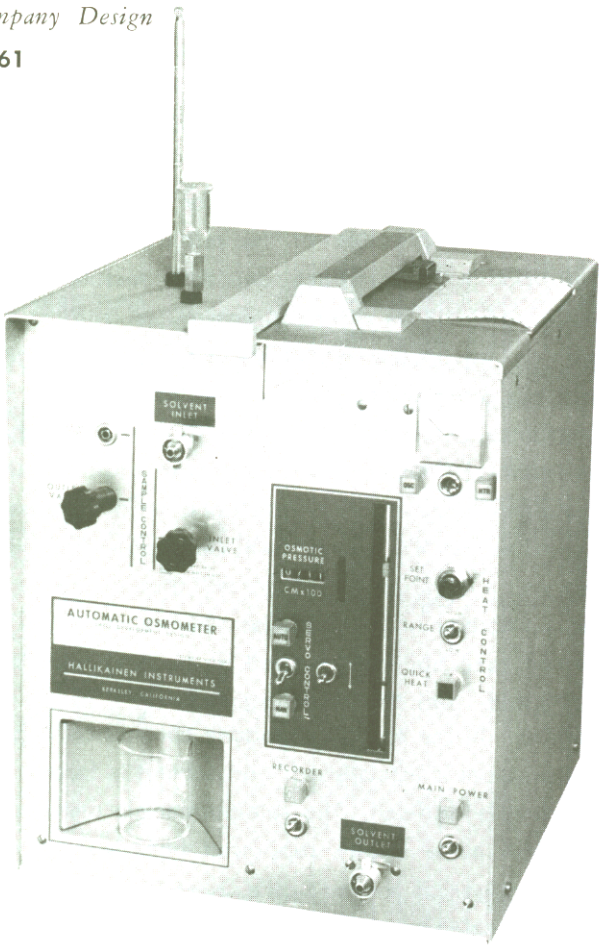
HALLIKAINEN *Instruments*
INDUSTRIAL and SCIENTIFIC
750 NATIONAL COURT, RICHMOND, CALIFORNIA, 94804

AUTOMATIC OSMOMETER

Shell Development Company Design

MODEL 1361



FEATURES:

1. Speed
2. Precision
3. Simplicity of Operation.
4. Direct Readout
5. Complete Record of Approach to Equilibrium
6. Easy Replacement of Solvent after Solute Permeation
7. Labor Saving
8. Compact
9. Operates up to 135°C

GENERAL

The photo above shows an AUTOMATIC OSMOMETER for the purpose of determining number-average molecular weights of polymers. When using this instrument, an operator need only pour a sample of 5 to 10 ml. into an external receptacle and then isolate it in the cell by means of the inlet and outlet valves. After a period of about 5 to 10 minutes the osmotic pressure can be read on a mechnical counter to one hundredth of a centimeter over a 10 cm. range. A built-in recorder, the pen of which is directly driven by the balancing servo mechanism enables the operator to observe the balancing process and to ascertain that equilibrium has been established; solute permeation can be detected by a decrease of osmotic pressure with time. The osmometer cell consists of two cavities separated by a semipermeable membrane. The bottom of the sample half-cell is formed by a thin metal diaphragm which responds to changes of volume. Displacement of this diaphragm due to solvent flow across the membrane is sensed as an electrical capacity change in an oscillator circuit, causing the servo mechanism to adjust the solvent head for zero osmotic flow. The speed with which this instrument makes a determination results not only in improved productivity but also in increased accuracy, because the error caused by small solute molecules permeating the membrane increases with time. These characteristics will enable osmometry to become a practical routine method for determination of number-average molecular weights of polymers.

PRINCIPLE OF OPERATION

Figure 1 shows the components of the cell block assembly. The grooved part of the sample half-cell (below the semipermeable membrane) is connected through a narrow bore with a shallow cavity whose bottom is formed by the pressure-sensing diaphragm.

The measurement of a series of osmotic pressures is preceded by a blank run (solvent on both sides of the membrane), to establish the zero point on the pressure scale; solvent is admitted to the sample half-cell and the sample valves are shut. If the sample at this moment still requires further heating to attain the preset temperature of the cell block, a volume expansion will take place, and the pressure-sensing diaphragm will be deflected downward from its null position towards a stationary electrode; this gives rise to a capacity change in an oscillator circuit. The imbalance of the oscillator then, via a servo mechanism, activates a mechanically driven plummet in a manometer tube in such a way that a negative pressure is exerted on the solvent half-cell above the semipermeable membrane. Solvent will then pass through the membrane until the excess volume, which in the present case has been caused by heating, has been dissipated, and the diaphragm restored to its null position. In the case of a volume contraction a positive pressure is established, and solvent is forced into the sample half-cell. The semipermeable membrane, although quite rigidly supported between the concentric ridges of the half-cells, is still slightly elastic so that under conditions of imbalance the pressure applied by the manometer is roughly proportional to the displacement of the diaphragm, thus preventing the servo from "hunting." The condition of equilibrium is then marked by

1. Zero deflection of the diaphragm
2. Zero net flow across the semipermeable membrane.

If now the same procedure is followed with a polymer solution instead of solvent in the sample cell, these two conditions can only be met if a negative manometer pressure is applied such as to prevent osmotic flow across the membrane; this, by definition, is the osmotic pressure.

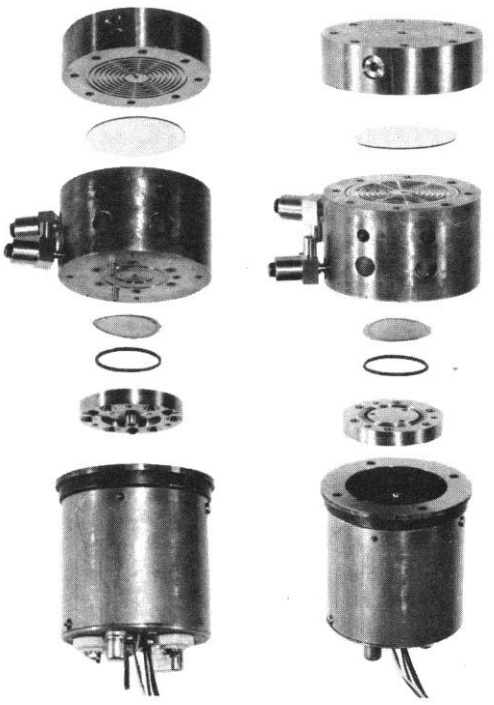


Figure 1

COMPONENTS

The pressure-sensing diaphragm is made of 0.0015 inch thick beryllium copper spaced 0.002 inch from the stationary electrode by means of synthetic rubies. Under operating conditions the diaphragm is displaced by only a fraction of one microinch. For this reason, and in view of the small osmotic flow across the membrane, it is of great importance to prevent erratic volume changes during a measurement. Constant temperature is therefore required, and particularly the rate of change of temperature has to be kept to a minimum. This is accomplished by an electronic thermoregulator employing a stable nickel resistance thermometer in a balanced bridge circuit. The bridge unbalance signal is amplified by a high-gain amplifier to control a pair of small thyratrons, which furnish a proportional current for maintaining

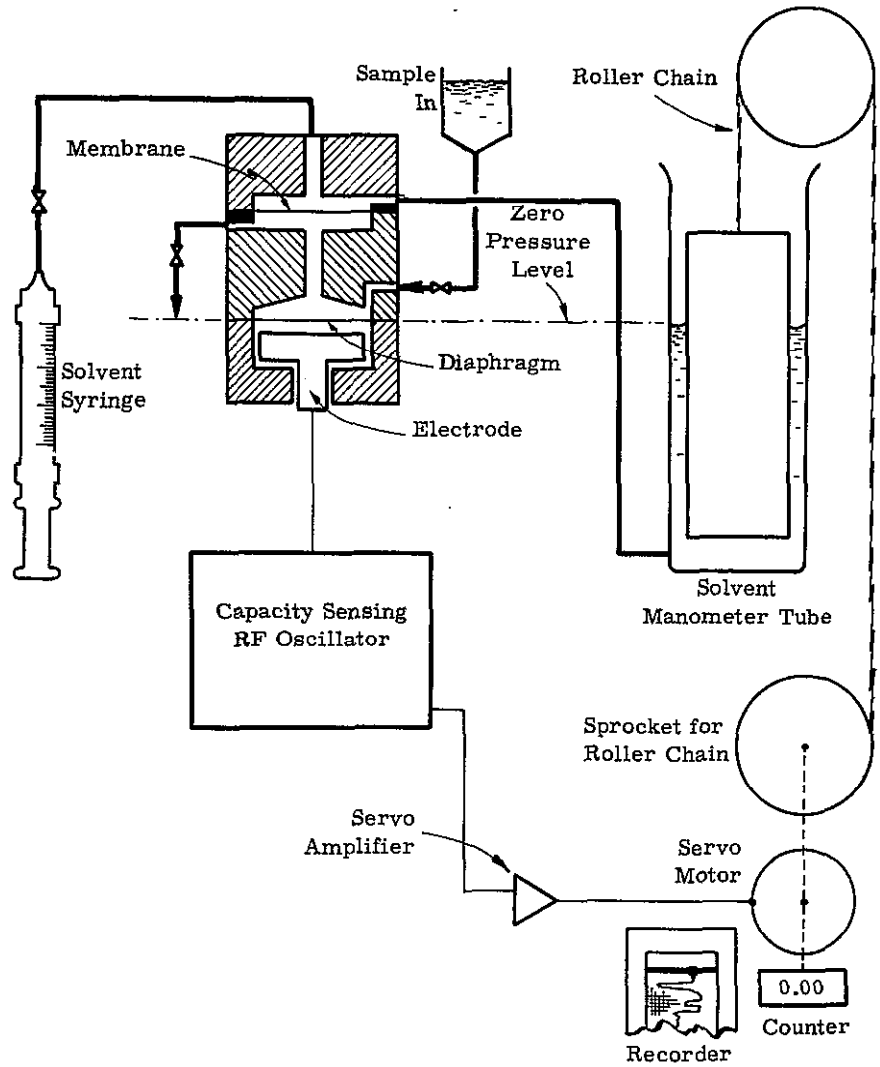


Figure 2 — Block Diagram

the cell temperature. The rate of change of temperature is held to less than 0.001°C per minute.

The capacity-sensing oscillator makes use of the rapid change in cathode current when the tank circuit of a quartz crystal oscillator is tuned through resonance. The overall sensitivity of the servo system is such that it operates on a deflection of 10^{-6} cm. at the center of the diaphragm corresponding to a cell volume change of approximately 10^{-3} microliter. This minute volume results, for example, from only 0.01 cm change of head in the solvent manometer. The oscillator circuit is temperature stabilized by use of self-compensating inductor, quartz-invar trimming capacitors, and a Nuvistor (TV type) oscillator tube.

The required highly precise control of cell temperature necessitates using a cell material having good thermal conductivity. Copper and aluminum alloy, both unsurfaced and hard chrome plated, have proved suitable for most applications. Development of cells of more corrosion resistant material is continuing. A small cell volume (less than 2ml.) contributes to the stability of the reading by minimizing the "thermometer effect." A rigid support of the semipermeable membrane to prevent ballooning is accomplished by the concentric grooves and lands in the half cells.

The sample valves have been carefully designed to be perfectly leak-tight so as to prevent undesired liquid flow. They are thermally close-coupled to the cell, and their volume is kept small to minimize their influence on the temperature stability of the cell.

The servo motor drives a miniature sprocket through gear reducers; direction and speed of rotation depending on the polarity and magnitude of the input signal from the oscillator. The sprocket drives a chain from whose end a metal plummet is suspended. Servo action lowers and raises the plummet in the manometer tube, and by doing so changes the solvent head in the manometer. The range of the manometer is between −1.0 and +9.0 cm. The zero point can be arbitrarily set by adding or withdrawing solvent through the solvent valves thus adjusting the blank reading to be near the zero point on the pressure scale. The negative range of −1.0 cm. provides the necessary driving force for recovery from any overshoot in the negative direction of the scale. This allows the measurement of osmotic pressures up to 9.0 cm. of solvent head.

The recorder pen is directly connected to the sprocket drive via a dial cable. The weight of the metal plummet effectively loads out any backlash in the servo gearing, thus producing a high resolution system.

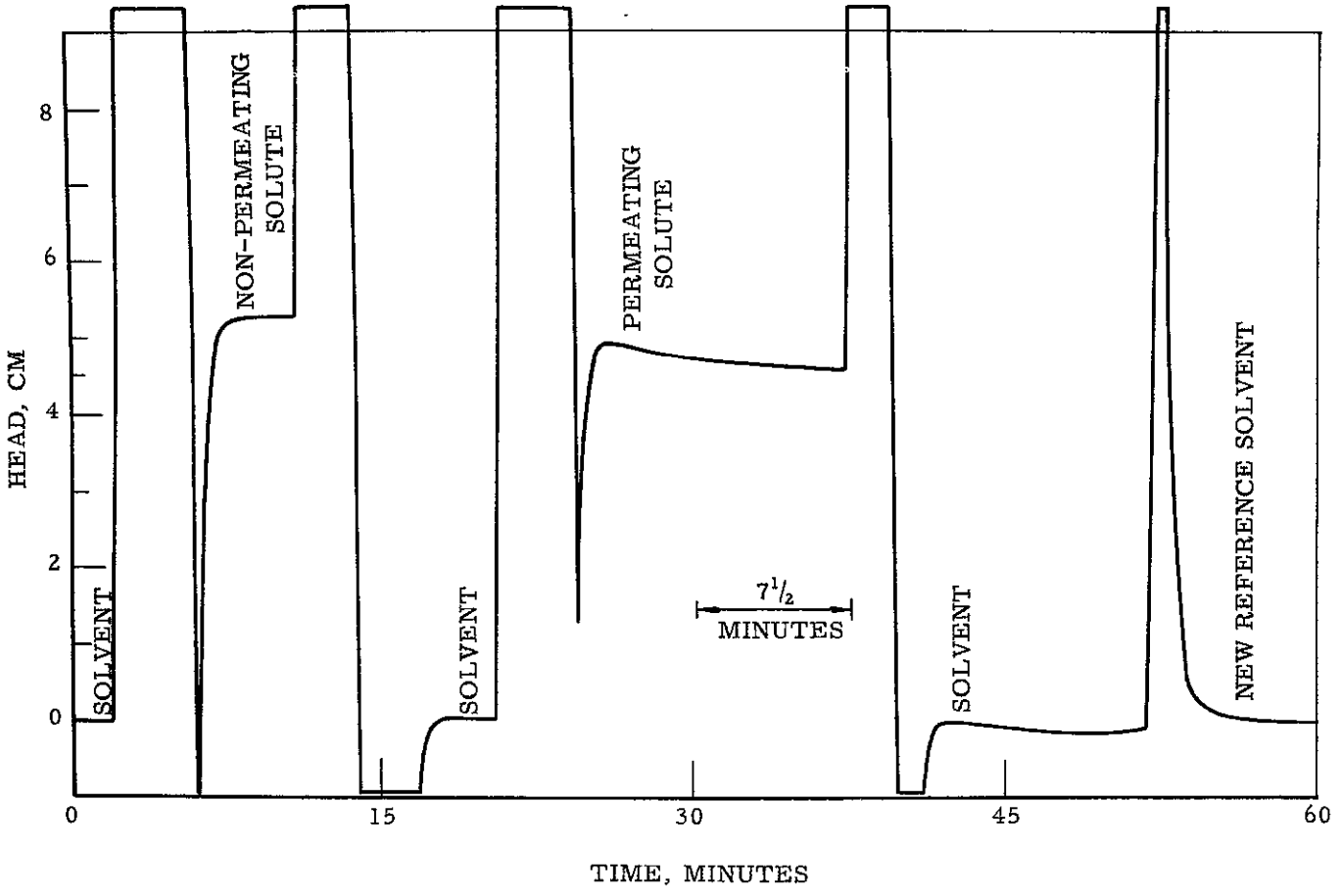


Figure 3 — Typical Recorder Chart (Continuous Chart Drive)

PERFORMANCE

The mechanical repeatability of the readings is ±0.01 cm. of solvent head. Under actual working conditions the repeatability may not equal this, depending on the quality of the membrane and the solvent-solute system.

Blank readings should be repeatable within ±0.02 cm. About 8 ml. of sample is required, 6 ml. of which is used to flush out the previous sample as it flows from the filling funnel on top of the instrument through the sample cell into the waste receptacle. By closing the valves at the appropriate time the last portion of the sample is isolated in the cell at atmospheric pressure.

SOLVENT RENEWAL

In the case of solute permeation through the membrane it is necessary to flush the solvent half-cell with fresh solvent after the determination. This is easily done by introducing solvent through the valve marked solvent inlet, and removing an equal volume through the solvent outlet valve, with the sample inlet valve open.

RANGE

Average number molecular weight range is between 5,000 and 500,000, depending on the membrane used.

SPECIFICATIONS

The standard model is capable of operating at any temperature from about 35°C. to 135°C. and the adjustment of temperature is continuous within this range. However, at operating temperatures above 60°C. approximately, it is necessary to use a heated sample funnel which is controlled by a thermoswitch at about the cell temperature. This accessory is available at extra cost.

Cabinet — 12" wide x 15" high x 13" deep

Weight — 50 pounds

Operation — 115 volts 60 cycle AC

Instrument contains the following sub assemblies: line voltage regulator, servo systems, mechanical counter, recorder, electronic thermoregulator, sample and solvent half cells, special sample valves, sensing diaphragm, membrane, capacity sensing oscillator, one chart roll, pen and ink set.