†Department of Pharmacy, University of Illinois at the Medical Center, Chicago, IL 60612
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▲ To whom inquiries should be directed.

TECHNICAL ARTICLES

Automated Drop Volume Apparatus for Surface Tension Measurement

E. L. ROWE

Abstract ☐ The drop volume method for surface tension measurements is ideal for new compounds since only a few milligrams are needed to obtain the CMC. However, the method is tedious and time consuming. An automated drop volume apparatus was constructed which provides sufficient accuracy with very little operator time. It is based on measurement of the average time between falling drops delivered from a constant-rate motorized syringe.

Keyphrases ☐ Surface tension measurement—automated drop volume apparatus ☐ Drop volume surface tension measurements—automated apparatus

Measurement of surface activity as a function of concentration usually requires upward of 500 mg. of compound when measured by the widely used du Nouy ring or Wilhelmy plate method. When the amount of test compound available is limited, the drop volume method is ideal since only a few milliliters of solution are required for accurate surface tension determination. However, this method is very tedious and time consuming. The present study was undertaken to automate the drop volume procedure so that very little operator time is involved while the minimum amount of test compound is used. Errors due to variation in operator technique also would be reduced. A prototype apparatus was built which fulfills these criteria.

An automatic drop counter was described by Nikita and Taubman (1). Refinements in the apparatus were made by others (2, 3). Essentially, it consists of a stalagmometer, photocell, light source, and appropriate electrical circuitry to count the *number* of drops formed from a measured volume. An apparatus has been constructed which automatically measures the *time* between drops at a constant delivery rate, permitting quick and direct calculation of surface tension.

APPARATUS

The essential features of the automated drop volume apparatus are shown in Fig. 1. It consists of a B-D syringe fitted with a special dispensing tip. The tip is a stainless steel cylinder which has a channel terminating at the lower end as a 26-gauge needle orifice. The lower end, upon which the droplets are formed, is machined flat and has a diameter of 0.6 cm. The syringe is held rigidly and discharged at a constant rate by a Harvard infusion pump.

A light source and photoelectric cell are fixed in a U-shaped metal holder so that an approximately 2 × 2-cm. light beam strikes the photocell. The photocell output is fed into a recorder[1] set for an input range of 10 mv.

After the syringe is filled with the test solution and it is installed in the pump, the motor is started and run continuously throughout the experiment. The combination of a 1/2-r.p.m. motor and 2-ml. syringe gives a measured delivery rate of 0.0332 ml. min.$^{-1}$. Droplets form on the tip, growing to a size that is dependent on the solution surface tension, and then fall off. As each droplet grows, it intercepts a significant portion of the light impinging on the photo-

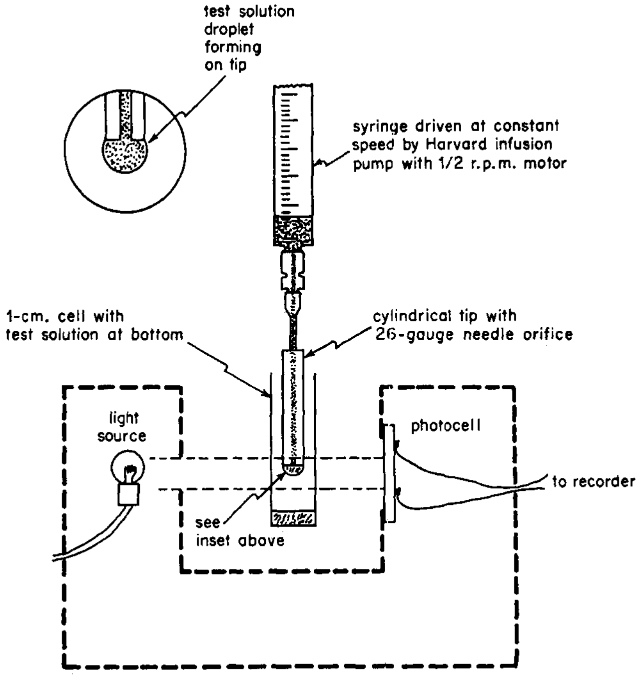

Figure 1—*Schematic of the essential features of the automated drop volume apparatus.*

[1] Sargent model SRL.

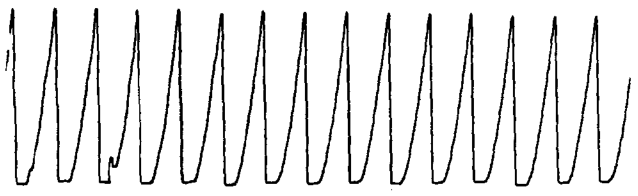

Figure 2—*Typical recorder tracing from automated drop volume apparatus.*

voltaic cell, gradually reducing the intensity of the signal to the recorder. At the instant the droplet falls, the electrical output of the photocell abruptly increases, producing a sharp spike on the recorder chart. Figure 2 illustrates a typical chart recording.

CALCULATION OF SURFACE TENSION

The volume of the drop is calculated from the average spike-to-spike distance, recorder chart speed, and delivery rate of the syringe. The total distance covered by n consecutive spikes is measured directly from the recorder chart paper and divided by $(n - 1)$ to get the average spike-to-spike distance. This value is divided by the recorder chart speed to obtain the time per drop and then multiplied by the syringe delivery rate to get the drop volume. The drop volume has to be corrected for the fraction left behind on the tip. The correction factor, θ, is calculated by means of the second-order polynomial (4):

$$\theta = 0.41344 \left(\frac{r}{V^{1/3}}\right)^2 - 0.70796 \left(\frac{r}{V^{1/3}}\right) + 0.90217 \quad \text{(Eq. 1)}$$

where r is the radius of the tip from which the drop hangs, and V is the volume of the falling drop. In this study, θ varies from about 0.600 for the smallest drops to 0.610 for the largest drops (water).

The surface tension, γ, is calculated using Tate's law (5) modified by the correction factor, θ:

$$\gamma = \frac{dVg}{2\pi r\theta} \quad \text{(Eq. 2)}$$

where V is the measured drop volume, d is the density of water (0.9970 g. ml.$^{-1}$ at 25°), g is the gravitational acceleration constant (980.6 cm. sec.$^{-2}$), and r is the radius of the tip. The γ values were actually obtained from a computer-generated table based on Eq. 2 with a radius of 0.300 cm.

INSTRUMENT PARAMETERS

The surface tension of compression-distilled water was measured repeatedly as a standard in CMC determinations. The temperature surrounding the apparatus was maintained at 25 ± 0.5°. The compression-distilled water used has a conductivity range of 0.3–2.0 μmhos. Table I contains a compilation of surface tension values measured over a period of 2 months. The average of 70.6 dynes cm.$^{-1}$ compares well with the accepted value of 72.0 (6) at 25°. The observed difference of less than 2% may be due to several factors, including water purity and instrumental vibration leading to premature drop release. Further refinements in the apparatus are planned which may improve the accuracy. In any event, the reproducibility and accuracy appear to be satisfactory for most purposes.

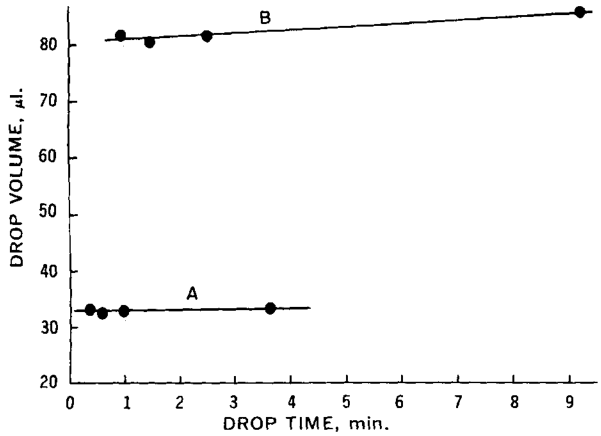

Figure 3—*Dependence of drop volume on drop equilibration time. Key: A, detergent solution; and B, water.*

Table I—Surface Tension of Compression-Distilled Water Measured by the Automated Drop Volume Apparatus

Run Number	Number of Drops	Average Volume/Drop, ml.[a]	Surface Tension, dynes cm.$^{-1}$
1	14	0.0850	72.1
2	10	0.0846	71.8
3	28	0.0830	70.5
4	18	0.0810	68.9
5	22	0.0830	70.5
6	18	0.0831	70.6
7	17	0.0827	70.2
8	23	0.0832	70.6
9	20	0.0833	70.7
10	22	0.0833	70.7
11	21	0.0833	70.7
12	33	0.0832	70.6
		γ average =	70.6

[a] Based on the measured delivery rate of 0.0332 ml. min.$^{-1}$.

Weiner and Zografi (4) found that the volume of a drop was independent of time if the drop was allowed at least 2 min. to form. Equilibration time apparently is not that critical in this apparatus. When the drop time (from beginning of drop formation to release) was varied over a range of from 0.3 to about 9 min., the drop volume was essentially unchanged for both water and a detergent[2] solution (Fig. 3). During normal operation the drop times ranged from 1 to 3 min.

Evaporation losses from the tip can cause errors in the drop volume measurement. By housing the syringe tip in a 1-cm. spectrophotometer cell, evaporation losses were minimized. It was found that the cell made a 4% difference in apparent drop volume at a drop time of 10–12 min. The data in Fig. 3 indicate that errors due to evaporation are negligible in the working range of 1–3 min.

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[2] Alconox is a highly surface-active laboratory detergent, blended from alkyl aryl sulfonates, sulfates, phosphates, and other additives.