What Makes a Good Drop Counter?

Titrations:

Titrations are widely used in analytical chemistry because it is quicker and less expensive to measure a volume than to measure a mass.   Volumetric glassware is much less expensive than a balance.

A standard solution of known molarity can be prepared with only one mass measurement.   Moles of titrant from this standard solution that are added to a reaction can then be calculated by a simple equation:

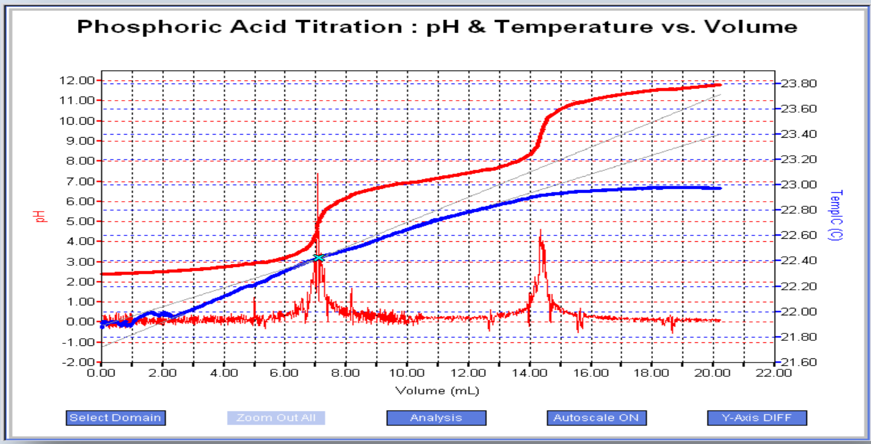
Moles = mL * moles/mL.

The most common type of titration is an acid-base indicator / equivalence point titration. It will tell us how much of the analyte is present when the indicator turns color.

However, there is a lot more information available if one is able to track and plot volume with respect to pH, temperature, conductance, or other solution properties.

The phosphoric acid titration curve presented in Figure 1 can be used to illustrate …

- The importance of choice of chemical indicators [you have to use a different indicator for each end point],
- The presence of buffer regions,
- The calculation of pKa, and
- The use of derivative plots to accurately locate end-points.



This phosophoric acid titration with NaOH took about 12 minutes and produced "text-book"data. Note the change in the slope of the temperature curve after the first end point.   The heat of reaction for neutralization of the first hydrogen is larger than that for the second hydrogen.

It also shows that the heat released during the reaction (blue line) is greater during neutralization of the first hydrogen than the second.

None of these concepts can be developed easily with a manual indicator / equivalence point titration.

Electronic Measurement of Volume:

pH and temperature are easy to measure electronically, but volume is not.

A peristaltic pump delivers a constant flow of titrant by moving a roller along a tube connected to the titrant reservoir, but is expensive and takes a fair amount of space on the lab bench.

Another way to measure volume is to create drops of constant volume, and count them.   A drop-forming tip fed by a constant-pressure-head reservoir will deliver drops of constant size.   One calibrates this system by counting the number of drops to fill a known volume - 330 drops to fill a 10.00 mL graduated cylinder, for example.   One can then measure volume by counting drops and multiplying by the calibration conversion factor:

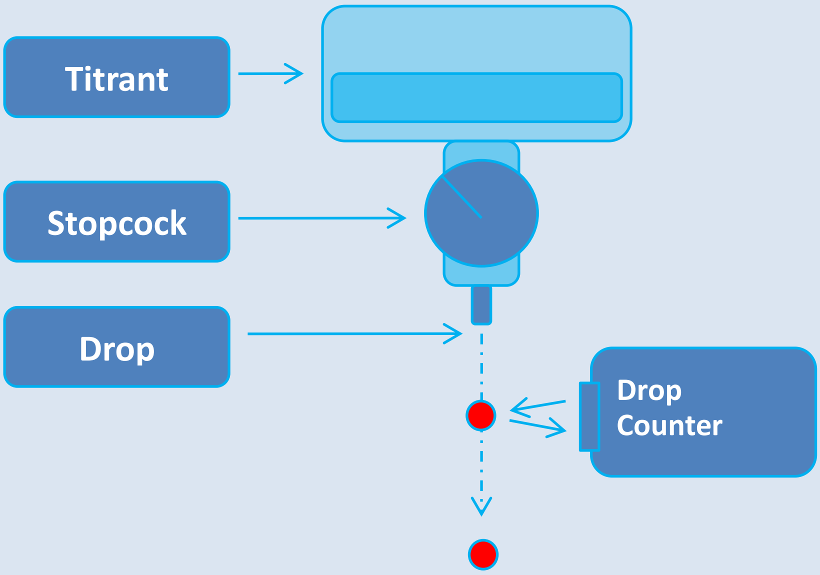
Conversion factor: 10.00 mL = 330 drops (10.00 mL/330 drops = 1).

mL = drops * (10.00 mL / 330 drops)

This system has some perils. If the pressure head changes much, both the drop size and drop formation rate will change. Drops can also fragment as they leave the drop-forming tip, causing additional false counts. But a drop generator is inexpensive and a drop counter is a lot less expensive than a pump.

A Little History:

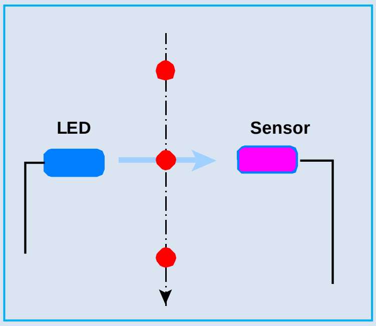
A review of the patent literature shows that drop counters have been around for quite a while. Their early development was in the medical field, to count drops in IV administration. A 1980 U.S. Patent (4,181,130) by Wilber Bailey described "*An electronic method and apparatus for evaluation of the quality of drop detection in apparatus for parenteral administration of medical fluids* ...".



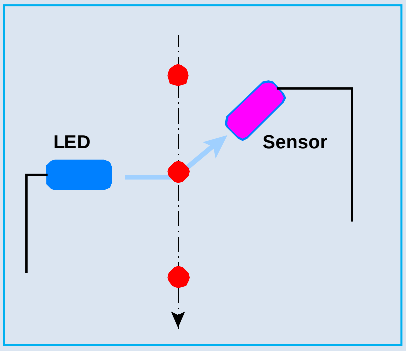
A drop counting system has three parts: A titrant reservoir, a drop generator, and a drop counter. The size of the drop is determined by the geometry of the drop-forming tip, the pressure head of the liquid above the tip, and the viscosity of the liquid. The MicroLab drop dispenser uses a wide, flat titrant reservoir to minimize the change of pressure head during a titration.

The first published educational application of a drop counter for chemical titrations was an article in the Journal of Chemical Education in 1991. [**Computer interfacing: A new look at acid-base titrations** John R. Amend , Kathleen A. Tucker and Ronald P. Furstenau, *J. Chem. Educ.*, **1991**, *68* (10), p 857].

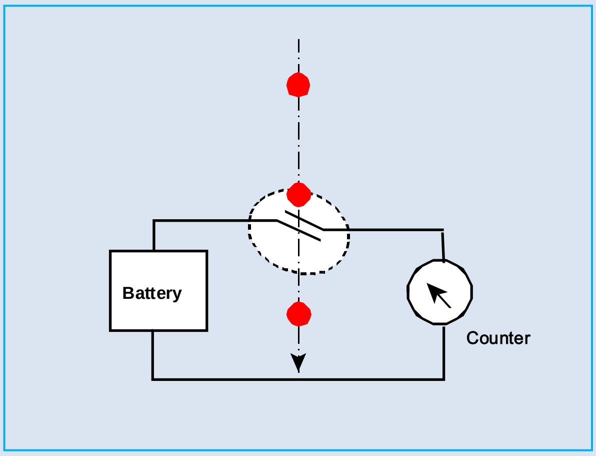
Kathy Tucker and Ronald Furstenau of the Amend research group at Montana State University developed and evaluated three types of drop counter for use in freshman laboratories.



Their first design used a light beam that was broken by a falling drop, similar to the Bailey patent, although the Bailey system also measured the size of the drop. In this design, it was very critical that the light beam strike the drop exactly the same way every time. The system would not count reliably if any part of the apparatus were bumped. In this system, drop detection was indicated by a decrease in light received at the sensor.



Their second design measured light refracted to the side as the drop passed through the light beam. In this design, drop detection was indicated by an increase over background light caused by the light refracted through the drop. Alignment was less critical, and counting was more reliable. However, both Design I and Design II were sensitive to changes in background light in the lab.



Their third design used the ionic character of the titrating solution to run the detector, which was simply two parallel nichrome wires spaced about 0.5 mm apart. The drop dispenser was aligned so that the drop fell between the wires, closing the electrical connection and causing a count. This design had no problems with background light, and was implemented in the MSU labs. However, it only worked with ionic titrants, and if the drop fragmented, all of the fragments were counted. The design was later sold by Montana State University to SCI Technologies, and was manufactured as part of the LabWorks system from 1991 to 2002.

Transmissive drop counters similar to the Tucker/Furstenau Design I are currently manufactured by three educational interface companies in the U.S.

MicroLab's Approach to Drop Counting:

Drop counters and an inexpensive constant volume drop dispenser are a useful and cost-effective alternative to burettes. They will not break and their resolution is about 50% better than a burette. And they do not get tired or distracted.

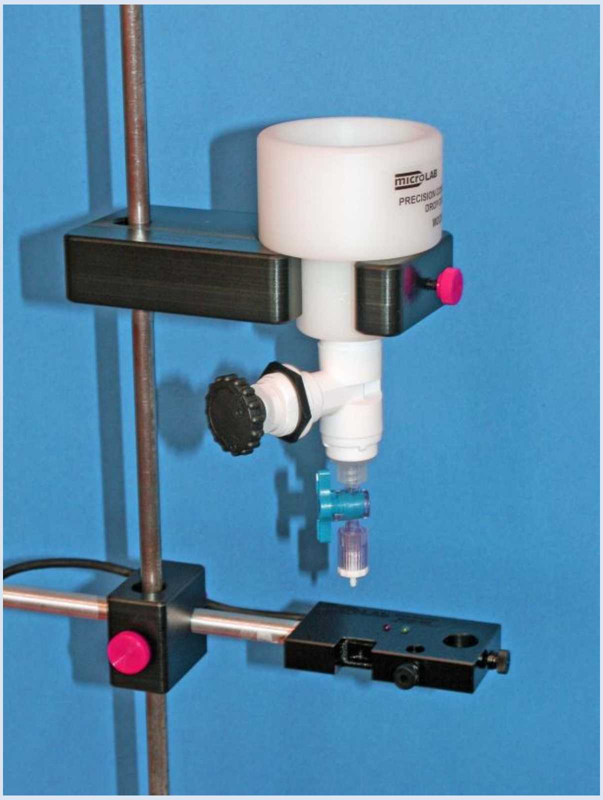
However, there are several perils in a volumetric drop counting system. MicroLab has developed a unique and extremely reliable drop counting system that was awarded a U.S. Patent in 2008. (# 7,414,255, Amend, Hammond, Hermens, Whitla).

Design criteria for the drop counter:

- **The counter must have a wide acceptance angle:** It must be able to detect drops that are not exactly aligned with the light beam. *MicroLab's patented Model 226 drop counter uses a reflective infra-red sensor that will count drops that pass anywhere through a sphere approximately 10 mm in diameter that is located next to the body of the drop counter. This makes it easy to set up.*

- **The counter must be immune to changes in background light**. Competing systems attempt to solve this problem by shielding the drop counter light path from outside light. *MicroLab's patented Model 226 drop counter background correction circuit measures and subtracts background light 8000 times per second, making the unit immune to changes in room lighting.*

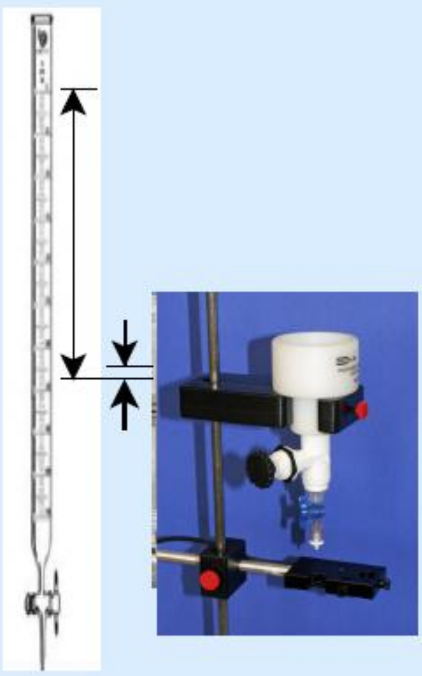
- **The counter must reject false counts from fragmented drops.** *MicroLab's patented Model 226 drop counter has an internal circuit that inserts a 25 millisecond "dead time" at the detection of each drop, eliminating false counts from fragmented drops.* It takes about 10 mS for a drop and its fragments to fall past the drop counter. Although this limits the maximum count rate to about 40 drops per second, aqueous drops coalesce into a stream at about eight drops per second and this limitation is not important.
- **The counter must be immune to chemical damage**. *MicroLab's patented Model 226 drop counter is made of chemically resistant Delrin and its electronics are potted in epoxy. It can easily withstand soaking over a weekend in 1 M NaOH solution, with no damage.*

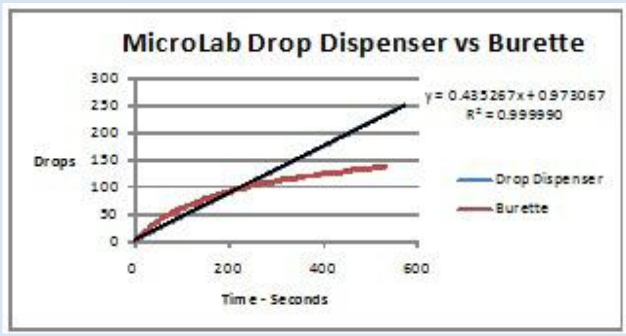


Design criteria for the Drop Dispenser:

- **For best resolution, the drop dispenser should produce small drops.** *MicroLab's drop generator tips produce drops of about 0.034 mL, or 34 microliters.* A burette produces drops of about 0.05 mL or 50 microliters.

- **The drop dispenser must produce drops of constant size and at a constant rate.** Changes in pressure head will change both the size of the drop and the rate of drop formation. *MicroLab's Model 154 constant volume drop dispenser has a large, shallow titrant reservoir that will dispense 30 mL with only 1 cm of change in pressure head.* For comparison, a burette dispenses 30 mL with about 32 cm change in pressure head.





- **The drop dispenser delivery rate must be easily adjusted**. An ordinary stopcock as on a burette or Leur fitting has a very small angle of motion between full on and off, and they stick. *MicroLab's Model 154 constant volume drop dispenser uses an industrial rotary needle valve to easily adjust drop rate. It uses a Luer stopcock to turn the system on and off after the desired drop rate is set.*

- **The drop dispenser should be unbreakable.** *MicroLab's Model 154 constant volume drop dispenser is made* *of nylon and polypropylene and is essentially unbreakable. If dropped on the floor directly on its tip, the Luer stopcock can break. It is easily replaced; a few spare stopcocks and tips are shipped with each order. Replacement cost for these parts is about $2.*

Important to accurate results are stir rate and solution mixing, the response time of the pH electrode (close to one second), and the reaction rate of the compounds involved. Strong acids react more quickly than weak acids. The result is that, if the drops are closer together than about 1.5 seconds, the pH reading does not reflect the true chemistry going on in the solution.

This classic strong acid / strong base titration used about 28 mL (900 drops) of base. The experiment took about 20 minutes.