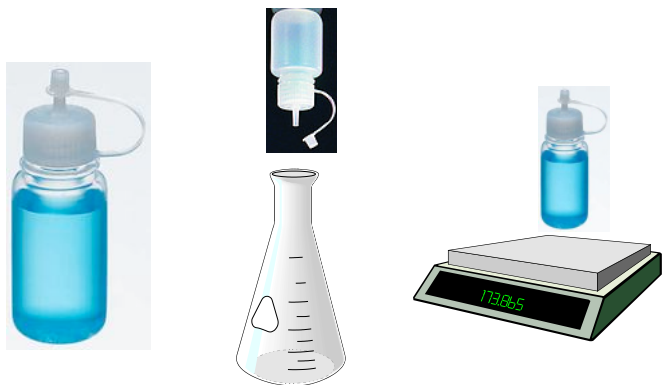


Gravimetric titration Part 1 – a simple, fast alternative to using a volumetric buret

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Introduction

Students can rapidly perform titration analysis experiments or rapidly measure points on a pH or potentiometric titration curve without having to use a volumetric buret. This can be accomplished by gravimetric (weight) titration, a technique in which a polymer drop-dispensing squeeze-bottle and a two-place top-loading balance take the place of a volumetric buret.



Gravimetric Titration with a Drop-Dispensing Squeeze-Bottle, an Erlenmeyer Flask, and a Two-Place Top-Loading Balance

A low-precision gravimetric titration can achieve the same reproducibility as a titration with a 50 mL volumetric buret. It requires less reagent quantities, it is faster and less complicated for the students and the teacher, and the equipment is far less expensive.

Part 1 of this article describes gravimetric titration in general, and presents a simple, low-precision gravimetric titration method, suited to secondary school use. Part 2 of the article, to be published later, will describe applying the method of gravimetric titration to determining the points on a titration curve of pH against added reagent quantity. Part 2 also presents the results of a head-to-head titrate-off precision comparison of a gravimetric titration and a volumetric titration of the same analyte.

Gravimetric Titration

According to Skoog, West, and Holler (1), there are three types of quantitative titrimetry: volumetric; gravimetric (weight); and coulometric. Gravimetric or weight titrimetry differs from volumetric titrimetry in that the amount of solution added to complete the reaction is measured by mass rather than by volume.

In a gravimetric titration, the titrating solution is contained in and dispensed from a small polymer drop-dispensing squeeze-bottle, fitted with either a glass or a polymer capillary tip. This is the gravimetric buret. Normal handling of the polymer bottle does not affect the mass of the bottle at the level of 1 mg (0.001 g).

With a modern direct-reading two-place top-loading balance, measurement of the dispensed mass of a solution with a gravimetric buret is very rapid and far easier to perform than the measurement of the dispensed volume of the solution using a volumetric buret. Gravimetric titrations with the same reproducibility can be performed much faster than volumetric titrations. Alternatively, one can obtain better reproducibility than is possible volumetrically, although this does require a higher-precision balance, more time, and more effort.

Super-High and High-Precision Methods

The drop size from the gravimetric buret, and the balance precision together determine the precision of the method. Guenther (2) describes a super-high-precision gravimetric titration method adopted by the U. S. National Bureau of Standards (NBS), where the result is reproducible to 1 part in 10,000.

Butler and Swift (3) describe a high-precision gravimetric titration method for undergraduate university students, where the results are reproducible to 1 part in 1,000 (compared to 3 parts in 1,000 with a volumetric buret). This is achieved by modifying a 60 mL polymer wash-bottle capillary tip to deliver smaller drops. Hawkes (4) and Ramette (5) provide further support for this methodology.

Skoog, West, and Holler (1) have described how to construct a gravimetric buret from a polymer storage bottle by gluing a buret glass capillary tip into an opening bored in the cap of the bottle.

A Simple Low-Precision Gravimetric Buret

An unmodified 50 or 60 mL polymer drop-dispensing squeeze-bottle (6) may be used as a gravimetric buret. The drop size from this bottle is about 25 drops per mL or gram (0.04 mL or 0.04 g), which is relatively too large for high-precision titrations, but the titrations are faster and more easily performed.

The cost of the 50 or 60 mL polymer drop-dispensing squeeze-bottles is much less than the cost of class B (student) 50 mL volumetric burets and buret stands and clamps (6, 7). The amount of storage space required is also reduced.

Used with a two-place laboratory balance, the results of gravimetric titrations performed with the squeeze-bottle buret will be comparable to, or better in reproducibility than, the use of a 50 mL volumetric buret.

Most titrant solutions used in secondary school chemical analyses may be placed in a polymer drop-dispensing squeeze-bottle without danger of reaction with the polymer.

Our experience with these bottles suggests that solutions (e.g.: 0.1 M NaOH, 0.1 M HCl, 0.01 M EDTA) may safely be left in the bottles for long periods without any problems.

By filling the bottles prior to the class, and refilling the bottles as necessary during the class, a teacher may both save on reagent wastage and allow more time for the student titrations.

Gravimetric Titration of Acidic Citrus Soft Drinks or Fruit Juices with 0.1 M NaOH Solution

Titration analysis of an acidic citrus soft drink (e.g., Sprite®) (8) or a fruit juice (e.g, President's Choice White Grape Juice) can serve as an example of a typical student gravimetric titration analysis. A sample of a carbonated drink must be heated in advance to remove the carbon dioxide gas, and then cooled.

Method:

1. Clean the required pipets, beakers, Erlenmeyer flasks, and drop-dispensing squeeze-bottles. Rinse with tap water, then distilled water.
2. (This can be done in advance by the teacher.) Rinse the gravimetric buret (a drop-dispensing squeeze-bottle) several times with small portions of standard 0.1 M NaOH solution. Fill the buret and replace the cap. Dry the outside of the bottle carefully.
3. Rinse a small beaker and the volumetric pipet several times with small volumes of the drink or juice, discarding the rinse portions (see Note a.). Take a sufficient volume of the sample solution into the beaker. Transfer the required portions into each of several Erlenmeyer flasks.
4. To each portion, add 2 - 4 drops of phenolphthalein indicator solution. Mix well.
5. Zero the two-place laboratory balance. Place the gravimetric buret on the balance. When the scale reading stabilizes, record the mass, in g units, to 2 decimal places.
6. Titrate over a white background, by adding drops of the NaOH solution to the first flask. Count drops, and swirl the solution in the flask to mix well. Be careful that no drops fall outside the flask, and keep the squeeze-bottle clean and dry.
7. Continue until a permanent pale pink colour remains for at least 30 seconds (see Note b.). Near the end of the titration, wash down the inside walls of the flask with a stream of distilled water from a wash-bottle. Record the drop count.
8. Zero the two-place laboratory balance. Place the gravimetric buret on the balance. When the scale reading stabilizes, record the mass, in g units, to 2 decimal places.
9. Repeat titrations, using the drop count from titration 1 as a guide to the end-point mass. Continue until three titrations agree within a range of 0.2 g or 0.3 g as instructed by the teacher.

Notes:

- a. All waste solutions may be safely put into a sink and washed away with tap water.
- b. When titrating a yellow fruit juice, the end-point colour will be pink with an orange background colour. The end-point colour change will not be sharp. Natural juices and wines are complex mixtures of components, with a slow change of pH at the end-point. Commercial analysis is performed with a pH meter to a pre-determined value (e.g.: 8.2 – 8.4 for wine) (9).
- c. No correction for the indicator blank has been applied. The indicator blank correction is less than one drop for the Sprite titration, and is difficult to determine for the coloured juice titration.
- d. Titrations of about 5 g (125 drops) are a good balance between precision (about 2 %) and tedium.
- e. For additional information about acids in fruit juices, see *Chem 13 News*, October 2006, pages 12-13, and April 2008, pages 4-6.

Typical Results:

Sprite®:

Replicate 10 mL samples. Four titrations.
Titration mass of 0.1 M NaOH solution (g):
2.45, 2.56, 2.51, 2.46 (65 – 70 drops per titration)
Mean = 2.50 g; % Rel. St. Dev. = 2.0 %

President's Choice® White Grape Juice:

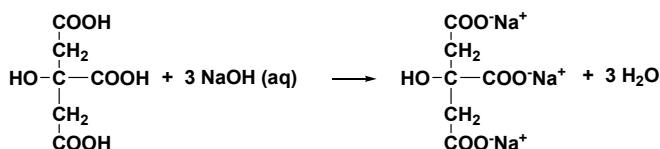
Replicate 10 mL samples. Six titrations.
Titration mass of 0.1 M NaOH solution (g):
5.19, 5.22, 5.13, 5.27, 5.20, 5.37 (120 - 130 drops per titration)
Mean = 5.23 g; % Rel. St. Dev. = 1.5 %

Titration Calculations:

Acid concentrations in drinks and juices are usually reported as either g / L or g / 100 mL (% w / v). For the Sprite, which is a synthetic drink, the only acid present is citric acid. For a grape juice, which is a complex mixture of many acids and other components, the titratable acid would be reported as an amount of "tartaric acid" as if that were the only acid present. For an apple juice, the result would be reported as "malic acid".

In order to complete the calculation, it is necessary to have a concentration value for the 0.1000 mol / L NaOH solution in units of mol / kg or mol / g. An estimate of this value as 9.96×10^{-5} mol / g has been made using a CRC Handbook value of 1.0039 g / mL for the density at 20 °C of 0.125 molar NaOH (10).

Calculation for Citric Acid in Sprite:

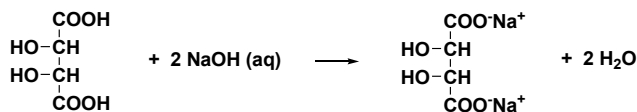


Citric Acid 192.1 g / mol

$$\begin{array}{l} \text{Citric Acid (g / L)} = \text{Mass (g) NaOH} \times \text{mol NaOH / g} \times \frac{1 \text{ mol CA}}{3 \text{ mol NaOH}} \\ \underbrace{\hspace{10em}}_{\text{Converts to mol NaOH}} \qquad \underbrace{\hspace{10em}}_{\text{Converts to mol CA}} \\ \text{(Citric Acid = CA)} \\ \times \frac{192.1 \text{ g CA}}{1 \text{ mol CA}} \times \frac{1}{\text{Volume (L)}} \\ \underbrace{\hspace{10em}}_{\text{Converts to g CA}} \qquad \underbrace{\hspace{10em}}_{\text{Converts to g / L CA}} \end{array}$$

$$\begin{aligned} \text{Citric Acid (g / L)} &= 2.50 \text{ g} \times (9.96 \times 10^{-5} \text{ mol / g}) \times (1 / 3) \\ &\times (192.1 \text{ g / mol}) \times (1 / 0.0100 \text{ L}) \\ &= \underline{1.59 \text{ g / L}} \end{aligned}$$

Calculation for Tartaric Acid in White Grape Juice



Tartaric Acid 150.1 g / mol

$$\begin{array}{l} \text{Tartaric Acid (g / L)} = \text{Mass (g) NaOH} \times \text{mol NaOH / g} \times \frac{1 \text{ mol TA}}{2 \text{ mol NaOH}} \\ \underbrace{\hspace{10em}}_{\text{Converts to mol NaOH}} \qquad \underbrace{\hspace{10em}}_{\text{Converts to mol TA}} \\ \text{(Tartaric Acid = TA)} \\ \times \frac{150.1 \text{ g TA}}{1 \text{ mol TA}} \times \frac{1}{\text{Volume (L)}} \\ \underbrace{\hspace{10em}}_{\text{Converts to g TA}} \qquad \underbrace{\hspace{10em}}_{\text{Converts to g / L TA}} \end{array}$$

$$\begin{aligned} \text{Tartaric Acid (g / L)} &= 5.23 \text{ g} \times (9.96 \times 10^{-5} \text{ mol / g}) \times (1 / 2) \\ &\times (150.1 \text{ g / mol}) \times (1 / 0.0100 \text{ L}) \\ &= \underline{3.91 \text{ g / L}} \end{aligned}$$

Additional Sample Types

Other synthetic drinks which may be analyzed for citric acid include all clear citrus-type carbonated soft drinks, and also "Kool-Aid®" type "Invisibles" drinks.

Other fruit juices which may be analyzed are: Apple juices, of which there are numerous kinds, including generic, low-acid, Macintosh, Granny Smith, etc., for malic acid; White cranberry juice for quinic acid. Vinegar may be analyzed for acetic acid content. Food vinegar is about 50 g acetic acid / L, and should be diluted 1 to 20 before taking a 10 mL sample for titration.

Summary and Conclusions

Unless the ability to care for and use a glass volumetric buret is one of the desired outcomes for the students, the gravimetric method has many advantages.

Comparison of Gravimetric to Volumetric Titration	
Pro	Con
- Inexpensive. Drop-Dispensing Squeeze-Bottles Cost Less than Volumetric Burets plus Stands and Clamps.	- Requires two-place laboratory balance(s).
- Less Reagent Amounts for the Same Precision.	- Impossible to "Split" Drops.
- Faster. No Buret Cleaning and Filling. Less Clean-Up.	- Physical Demand of Squeezing Drops out of a Bottle.
- Easier. No Buret Reading.	- Tendency to Lose Concentration and Allow Drops to Fall Outside the Flask.

Gravimetric titration using a polymer drop-dispensing squeeze-bottle as a gravimetric buret will allow your students to do more titration analysis exercises in less time than volumetric titration with a glass volumetric buret. You will, however, need one or more two-place laboratory balances, depending on the physical layout of your classroom and the number of students.

The amount of student training required for the gravimetric method is less, and it is easier and faster. The student time required to prepare for, carry out, and clean up after the titrations is reduced relative to a volumetric method.

The amount of reagent required for a gravimetric titration is less than that required for a volumetric titration. Students will obtain roughly the same precision on a "5 g" gravimetric titration by using a two-place balance as they will on a "10 mL" volumetric titration by using a 50 mL volumetric buret. The question of the relative precision of the volumetric and gravimetric methods will be addressed in Part 2 of the article.

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