Gravimetric titration Part 2 – a pH titration curve; a precision comparison to volumetric titration

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Introduction

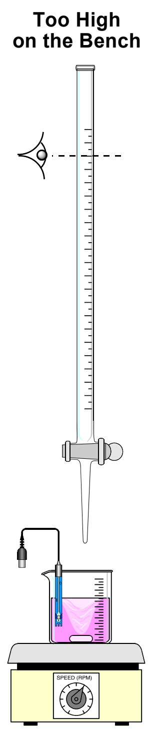
By the method of gravimetric titration, using a polymer drop-dispensing squeeze-bottle as a gravimetric buret, students can rapidly perform titration analysis or rapidly measure the points on a pH or potentiometric titration curve without having to use a volumetric buret. Part 1 of this article (*Chem 13 News*, month, year, pages.) described gravimetric titration in general, and presented a simple, low-precision gravimetric titration method, suited to secondary school use.

This Part 2 of the article describes how to use a gravimetric titration to measure the points on a plot of pH against added reagent quantity (a pH titration curve). Also, the results of a head-to-head precision titrate-off between the gravimetric and volumetric titration methods will be presented.

Gravimetric pH Titration Curves

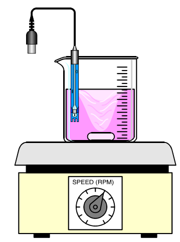
The gravimetric titration method is well suited to the manual development of a pH or other potentiometric titration curve. Two important factors here are the physical simplicity of the method, and the ease with which the titrant solution may be metered into the titration vessel. A concrete description, of a before and after case from our second term analytical chemistry laboratory for the two-year technician program, will be used to illustrate these points.

Previously, the students were asked to use the volumetric method to record the titration curve of a solution containing an unknown concentration of carbonate and bicarbonate ion. Although they were familiar with the use of a stirring motor and PTFE-coated stirring-bar, a combination electrode, and a pH meter, they had difficulty putting the 50 mL volumetric buret in place over the titration beaker.

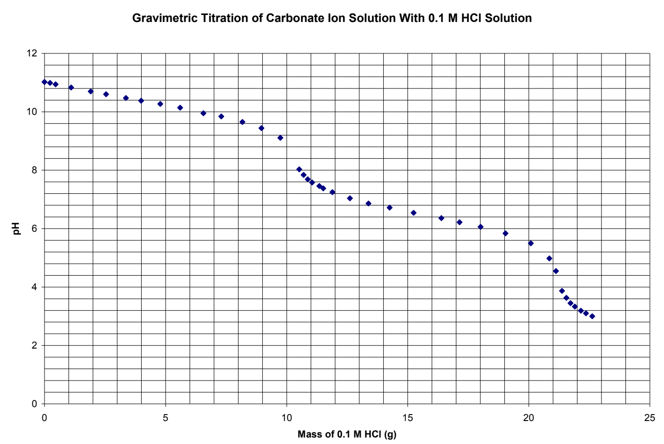


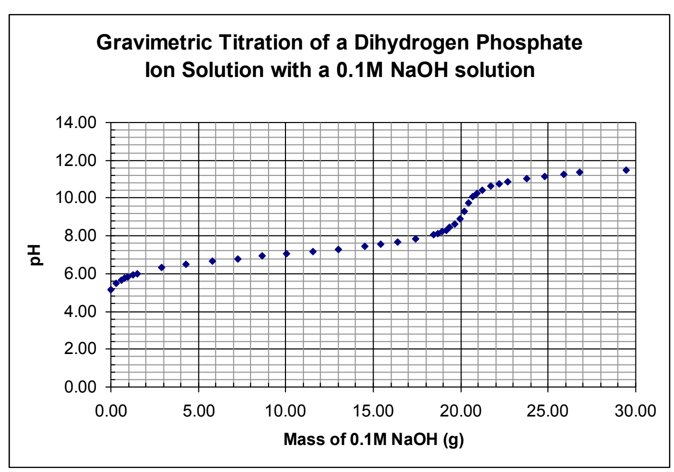
They then had great difficulty getting up high enough over the bench to read the level in the buret, and found it nearly impossible to control the small additions of titrant desired for the titration curve measurements. The exercise was overlong for a 2 hour period; it was hazardous because the students were climbing up on the bench to read the buret; and the titration curves produced were of poor quality.

Switching to the gravimetric titration method solved these problems. Using a polymer drop-dispensing squeeze-bottle as a gravimetric buret allowed the titrant solution to be easily metered directly into the beaker by counting drops. The mass of the added reagent was determined by measuring the mass of the squeeze-bottle after each addition on a two-place top-loading balance. When the pH was changing slowly, more drops (e.g. 30 drops), and when the pH was changing rapidly, less drops (e.g. 5 drops) were added between successive pairs of pH - mass measurements.



It was found that in the same 2 hours of laboratory time, two different pH titrations curves of good quality could be determined (1), even by students with little experience, as illustrated by the student plots shown.

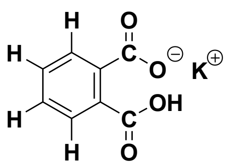




Comparison of the Precision of a Gravimetric and a Volumetric Titration

How does the precision or reproducibility of the two methods – gravimetric titration and volumetric titration – compare?
Can you be confident in switching to the gravimetric method? This can be answered by a simple experiment. The accuracy of the methods is a more difficult question, which cannot be determined simply.

A comparison of the precision of the two techniques was made by using both to standardize approximately 0.1 M sodium hydroxide (NaOH) solutions with primary standard solid potassium hydrogen phthalate (KHP).



Potassium Hydrogen Phthalate

KHP: $KC_8H_5O_4$ = 204.2 g / mol

$$KC_8H_5O_4\,(aq) + NaOH\,(aq) \rightarrow NaKC_8H_4O_4\,(aq) + H_2O$$

The weighings of the solid KHP were made with a four-place analytical balance because the mass of dried KHP required in each titration was small. The indicator was phenolphthalein. The indicator blank correction was determined to be 0.04 mL for the volumetric method and 0.04 g for the gravimetric method.

Volumetric Titrations of KHP

Six volumetric titrations were performed, using approximately 0.35 g of KHP in each trial, titrating with the NaOH solution from a 50 mL volumetric buret. The titrations were about 18 mL in volume. The individual result of each titration was calculated as shown. The mean molarity of the NaOH solution was determined to be 0.09468 mol NaOH / L. The relative percent standard deviation was 0.41 %.

$$\text{mol / L of NaOH} = \underbrace{\text{mass of KHP (g)} \times \frac{1\text{ mol}}{204.2\text{ g}}}_{\text{Converts to mol KHP}} \times \underbrace{\frac{1\text{ mol NaOH}}{1\text{ mol KHP}}}_{\text{Converts to mol NaOH}}$$

$$\underbrace{\times \frac{1}{\text{Corrected Vol (mL)}} \times \frac{1000\text{ mL}}{1\text{ L}}}_{\text{Converts to mol / L of NaOH}}$$

Gravimetric Titrations of KHP

Eight gravimetric titrations were performed, using approximately 0.24 g of KHP in each trial, titrating with the NaOH solution from the polymer drop-dispensing squeeze-bottle. The titrations were about 12 g in mass. (This is about 300 drops, which is very tedious.) The individual result of each titration was calculated as shown. The mean mol / kg of the NaOH solution was determined to be 0.09683 mol NaOH / kg. The relative percent standard deviation was 0.28 %.

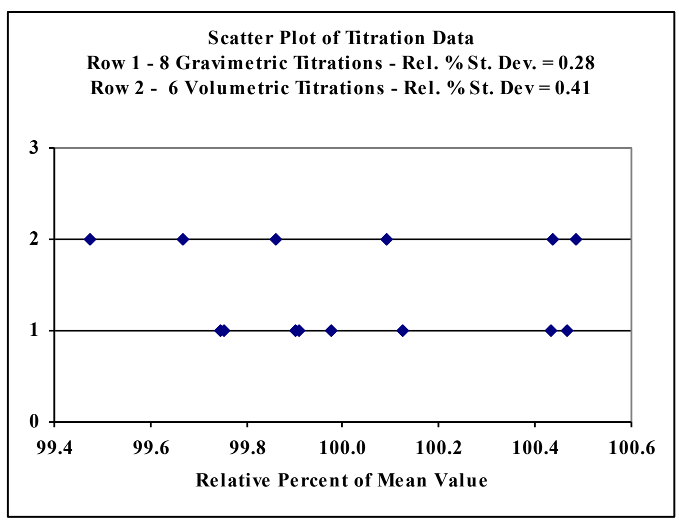
$$\text{mol / kg of NaOH} = \underbrace{\text{mass of KHP (g)} \times \frac{1\text{ mol}}{204.2\text{ g}}}_{\text{Converts to mol KHP}} \times \underbrace{\frac{1\text{ mol NaOH}}{1\text{ mol KHP}}}_{\text{Converts to mol NaOH}}$$

$$\underbrace{\times \frac{1}{\text{Corrected Mass (g)}} \times \frac{1000\text{ g}}{1\text{ kg}}}_{\text{Converts to mol / kg of NaOH}}$$

Comparison of the Results and Conclusion

A graphical presentation of the results of the comparison is shown. Within each set, each individual result has been plotted as a percentage of the mean value of the full set.
The reproducibility of the result is better for the gravimetric titrations than for the volumetric titrations even though the mass of KHP used in each titration was larger for the latter. The full data set of the comparison is available as an Excel file by e-mail request.

The result indicates that you may be confident in using the method of gravimetric titration with your students.



Reference

1. Cash, D., Experiments Page, Experiment 7, pH Meter: http://www.uclmail.net/users/dn.cash/experiments.html