Gravimetric Titrations are More Accurate, More Precise, and Easier than Volumetric Titrations

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Abstract

Gravimetric titrations were compared statistically in this study with volumetric titrations. A sodium hydroxide solution was standardized with pure potassium hydrogen phthalate (KHP). This solution was then used to analyze an impure sample of KHP with a known concentration. The procedure was conducted by the gravimetric and volumetric titration methods. The calculated results of each titration method were statistically compared to determine which method was more accurate and/or precise. In addition, the uncertainties present with each method, including buret delivery precision and weighing precision were evaluated. Last, the two techniques were performed by an entire class of upper-division analytical chemistry students, and the results were analyzed for accuracy and precision. The findings illustrated that gravimetric titrations were more accurate, precise and much easier to use compared to volumetric titrations.
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Introduction:

Throughout the past 150 years, titrations have become an important method in the scientific world. They are used in a variety of different chemical and biological procedures and are a common method used in science to determine the unknown concentration of an analyte. Classic titrations performed in laboratories include acid-base titrations, redox titrations, electrochemical titrations, and Kjeldhal titrations. A titration was first defined in 1855 by German chemist Friedrich Mohr as the “weighing without scale” method. He labeled a titration in this way because of the lack of instrumentation that is used when performing a titration.\(^7\) One such process is to determine the precise amount of chemicals and preservatives found in everyday food and pharmaceutical medicines. Environmental chemists use titrations to determine hazardous metal concentrations in water samples collected from surrounding areas of mines and power plants.\(^6\) Acid-base titrations are used to test the acidity or alkalinity of solutions. This is advantageous when making products such as wine or biodiesel. Titrations are an important method used in the scientific world because they are relatively easy to perform and are an accurate and precise way of completing scientific experimentation.

When performing a titration, a known concentration of analyte is placed into a beaker and thoroughly dissolved. A titrant solution is made and is then transferred, through many different methods, into the beaker containing the analyte and a specific indicator. The titration is completed once the theoretical equivalence point is reached. The equivalence point is reached when the amount of titrant is stoichiometrically equal to the amount of analyte originally present in the solution. With this, the unknown concentration of the titrant can be determined. The equivalence point is determined by
observing the end point, which is the change seen by the indicator. To complete a high-quality titration, the amount of titrant must be measurable and variable. In a titration, the more easily and more reproducibly a very small volume of titrant can be added, the more accurate and precise the results will be.\(^4\) There are two ways of measuring the titrant, by mass or by volume, and these are referred to as gravimetric and volumetric titrations.

Volumetric titrations have been used over the past 100 years of analytical chemistry due to their ease of use. Experiments with volumetric burets and titration procedures have led to the development of a simplistic glass buret and a titration method.\(^1\)\(^8\) Regardless of the popularity of volumetric titrations, there exist many potential sources of error in the volumetric titration method. The first difficulty with volumetric titrations is determining the volume at the meniscus. Estimating the meniscus is difficult, subjective, and prone to variability from scientist to scientist.\(^1\)\(^5\)\(^8\) Another problem with volumetric titrations is the control of the stopcock, which is placed on the end of the buret and which controls the delivery of the titrant solution to the analyte solution. To achieve complete control of the stopcock takes a great amount of practice, especially when controlling partial drops.\(^1\)\(^5\)\(^8\) The third major problem with volumetric titrations is the necessary ratio of total buret volume to graduation size, typically 500:1. The buret also has to drain perfectly cleanly during a titration. If a small volume of titrant sticks to the side of the buret, the resulting error can be relatively large, as the undelivered titrant is recorded as having been transferred to the analyte flask.\(^1\)\(^8\)

Gravimetric titrations have also been known for more than a hundred years; however they have never become as popular as volumetric titrations. Historically, one of the disadvantages of gravimetric titrations was the required use of an analytical balance.\(^8\)
Analytical balances with an accuracy of 0.1 mg are used to measure the amount of analyte that is used. Until very recently, these balances were extremely expensive, time-consuming to operate, and required a skilled analyst to use. The digital analytical balances used today are very easy and quick to use. Although analytical balances are still fairly expensive, between $2,000 and $4,000, their usage is spread out among many applications in a typical laboratory. In an academic laboratory, a single balance may be shared among a large number of students, whereas a large number of burets would be required for the same number of students. Another historical disadvantage with gravimetric titrations was that no device existed that could be both easily weighed and that could deliver titrant precisely. To solve this problem, simple, inexpensive plastic containers with fine tips are now available for use. These fine gravimetric titrators can cheaply be made from easily available materials. Many other difficulties associated with volumetric titrations are eliminated in gravimetric titrations. For example, the leakage that occurs with the connection of the stopcock and the volumetric buret is eliminated with gravimetric titrations. The gravimetric titrator allows for no leakage, which results in more accurate results. Another common problem with volumetric titrations is the reading of the meniscus. Using the gravimetric titration, there is no subjective reading of the meniscus since the amount of titrant is measured by mass not volume. Another disadvantage to the volumetric buret is the calibration of the buret. Each graduation displayed on the buret may not be evenly spaced. In order to make up for this, the volumetric buret must be calibrated to determine the actual volume delivered by the buret over the entire volume range of the buret. With gravimetric titrations, there is no need to calibrate the buret. Rather it is the analytical balance that is calibrated in a
procedure that typically takes a few seconds.\textsuperscript{1,8} The cost for each method is extremely different. The price for a decent, accurate buret ranges can be more than $200, while a gravimetric buret can be assembled for less than a dollar. As a result, in academic laboratories, significant cost savings can result if a switch is made from volumetric to gravimetric titrations.\textsuperscript{1,2,5,8} One of the most common problems with volumetric burets is trying to keep them clean and free of debris. A new, clean buret will last for a while; however with sodium hydroxide as the titrant, the glass will eventually start to corrode, causing etching to occur. This will, in turn, cause drops of titrant to stick, resulting in inaccurate volume deliveries from the buret.\textsuperscript{2,5} With the use of plastic gravimetric burets, the sodium hydroxide titrant will not be able to corrode the buret, thus lessening the possibility of error. With all the advantages to using gravimetric titrations, however, they do not exist without error. One problem associated with the gravimetric buret is the possibility for evaporation of the titrant that might occur at the tip. Nevertheless, the rate of evaporation would be expected to be very slow. Another difficulty associated with the gravimetric titrations is the potential for leakage of small drops from the tip of the gravimetric titrators. To eliminate this, it is best to keep the gravimetric titrator free of titrant until it is needed and to be careful when handling it when it is filled with titrant.

The present study analyzes the statistics associated with volumetric and gravimetric titrations and demonstrates that gravimetric titrations are easier to use, more accurate, and more precise than volumetric titrations.
Experimental:

Equipment:

A gravimetric buret was constructed using a 125 mL Nalgene wash bottle and a disposable graduated polyethylene pipette (Fisher, cat# 13-711-9AM). The pipette had a bulb volume of 3.3 ml. Using a Bunsen burner, the pipette tip was warmed and drawn out into a fine capillary to create a micro titrator. The drop volume from the micro titrator was less than 10 μL. The micro titrator was fitted snugly into a hole that was drilled into the cap of the wash bottle. The gravimetric buret with micro titrator is shown in Figure 1. The micro titrator is shown in Figure 2.

Figure 1. Gravimetric buret
A Sartorius Acculab balance (ALC 210.4, capacity 210 g, precision 0.1 mg) was used to accurately weigh every sample used for all experiments.

The borosilicate glass volumetric buret (KIMAX 17021H-50) was used for the volumetric titrations. The total capacity of the volumetric buret was 50 mL marked with 0.1 mL graduations. A PTFE stopcock was used in order to control drops.

**Chemicals:**

Potassium hydrogen phthalate (Certified ACS grade, Assay; 100.01%, Fisher Scientific) that was dried at 120 °C for two hours then cooled in a desiccator was used as the acidometric standard. Sodium hydroxide (NF/FCC grade, Fisher Scientific) was diluted to approximately 0.11 M with CO₂-free deionized water. The sodium hydroxide solution was used in the gravimetric buret, with the micro titrator used to deliver the partial drops of titrant when needed.
Solid samples of 40-60 wt% potassium hydrogen phthalate (Thorn Smith Laboratories, Beulah, Mi) were used as the unknowns in the experiment. The weight percent of each unknown was known to the nearest 0.01%.

Solid phenolphthalein (J.T. Baker Chemical Co. Baker analyzed) was dissolved in 50/50 ethanol/water and diluted to a concentration of 0.5 mg to formulate the indicator.

**General Procedure:**

The analyte was prepared by accurately weighing ~0.5 g potassium hydrogen phthalate (KHP) and dissolving it in ~25 mL CO$_2$-free deionized water and adding three drops of the phenolphthalein indicator. The NaOH solution was added to the gravimetric buret and was weighed using the balance to the nearest 0.0001 g. This solution was standardized by adding it quickly from the gravimetric buret to the solution containing the weighed KHP until the pink color persisted in the solution for 1-2 seconds. For the rest of the titration, the NaOH titrant solution was delivered dropwise by the micro titrator until the end point was reached, which was represented by the slightest pink color change of the analyte solution. This process was repeated four times in order to determine the hydroxide of the titrant. The solution concentration was quantified by dividing the moles of hydroxide by the mass of the titrant. This ratio was known as the “Molamity” \( \bar{M} \). \( \bar{M} \) is defined to be \( \frac{\text{mnoles OH}^-}{\text{g solution}} \) or \( \frac{\text{mol OH}^-}{\text{kg solution}} \). The standard deviation and the percent relative standard deviation were also calculated. Once the NaOH solution was standardized, the weight percent of an unknown concentration of KHP was determined.
**Results and Discussion:**

In order to determine the accuracy and precision for the calculations of each titration method, the theoretical precision and possible uncertainties were established. The precision of the volumetric buret was calculated to examine the variability in titrant delivery relative to a typical total titrant volume. The delivery volume uncertainty of the volumetric buret was determined by testing the exact amount of liquid dispensed by the buret for a series of five apparent deliveries of 20 mL. In order to calibrate the volumetric buret, what was read to be 20 mL was dispensed into an empty, previously weighted Erlenmeyer flask. The flask was then weighed again using the analytical balance. The mass of the flask was then converted to mL by using the density of water at 22 °C. The final volume was determined to be the actual volume dispensed from the buret. The results are shown in Table 1.

**Table 1. Volumetric Buret Delivery Precision**

<table>
<thead>
<tr>
<th>Trial</th>
<th>Apparent Volume Delivered at 22°C (mL)</th>
<th>Measured Mass Received (g)</th>
<th>Density-Corrected Volume Received (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.00</td>
<td>19.8999</td>
<td>19.949</td>
</tr>
<tr>
<td>2</td>
<td>20.00</td>
<td>19.8830</td>
<td>19.932</td>
</tr>
<tr>
<td>3</td>
<td>20.00</td>
<td>19.9358</td>
<td>19.980</td>
</tr>
<tr>
<td>4</td>
<td>20.00</td>
<td>19.9736</td>
<td>20.018</td>
</tr>
<tr>
<td>5</td>
<td>20.00</td>
<td>19.9852</td>
<td>20.030</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>19.9818</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td>0.04205</td>
</tr>
</tbody>
</table>

The uncertainty in the volumetric delivery was quantified by the standard deviation, 0.04 mL. Using this uncertainty through the calculations in determining a typical unknown weight percent of KHP, a ±0.12% error is already present.
The typical uncertainties in measurement that could have been present during a classic titration calculation were determined. Each uncertainty was compared for both volumetric and gravimetric titration calculations. The results are shown in Table 2.

**Table 2. Sources of Uncertainty in a Typical Titration Calculation**

<table>
<thead>
<tr>
<th></th>
<th><strong>Gravimetric</strong></th>
<th><strong>Volumetric</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Typical Mass KHP</strong></td>
<td>0.4000 ± 0.0001 g</td>
<td>0.4000 ± 0.0001 g</td>
</tr>
<tr>
<td><strong>Typical Amount of Titrant</strong></td>
<td>20.000 ± 0.0001 g</td>
<td>20.00 ± 0.04 mL</td>
</tr>
<tr>
<td><strong>Relative Uncertainty</strong></td>
<td>1 part in 4000</td>
<td>1 part in 500</td>
</tr>
</tbody>
</table>

Each uncertainty was determined for a typical titration in which 0.4 mg KHP was titrated with 20 ml of approximately 0.1 M NaOH (0.1 $M$). The most significant uncertainty in a volumetric titration dealt with reading the volume of titrant delivered while the most significant uncertainty in a gravimetric titration was the mass of the KHP. With the overall uncertainties, there is almost a ten-fold difference between the inherent errors associated with volumetric titrations versus gravimetric titrations. It can be seen that the uncertainty associated with volumetric titrations derives from the delivery of the titrant, which is dependent on the experience of the analyst and the quality of the buret. In contrast, the uncertainty correlated with the gravimetric titrations is due mostly to weighing the KHP, and directly related to the mass discrimination of the analytical balance.

In order to compare the accuracy and precision of the two techniques, the mass percent determinations for a sample of KHP of an unknown weight percent were
determined using both gravimetric and volumetric titration methods. The statistical results are shown in Table 3.

**Table 3. Mass Percent KHP in a Commercial Unknown Sample (50.95 wt% KHP)**

<table>
<thead>
<tr>
<th></th>
<th><strong>Gravimetric</strong></th>
<th><strong>Volumetric</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean</strong></td>
<td>51.12%</td>
<td>50.60%</td>
</tr>
<tr>
<td><strong>Absolute Error</strong></td>
<td>0.17</td>
<td>-0.35</td>
</tr>
<tr>
<td><strong>STDEV</strong></td>
<td>0.158</td>
<td>0.822</td>
</tr>
<tr>
<td><strong>PRSD</strong></td>
<td>0.309</td>
<td>1.625</td>
</tr>
<tr>
<td><strong>Number of Trials</strong></td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3 shows that the gravimetric titration method produced a smaller absolute error value, meaning that the calculated mass percent values of KHP were very close to the mean value. In addition, the precision of the gravimetric titrations was better, as evidenced by the smaller standard deviation.

These results were determined after a considerable amount of practice with both titration methods. In order to really test the hypothesis of which method is truly more accurate and precise, a lab was designed to be performed by twenty-six inexperienced analytical chemistry students in the spring 2010 Quantitative Analysis class at Carroll College. Each student was given a sample with an unknown weight percent and asked to identify the weight percent of his or her individual unknown. The general procedure was similar for both gravimetric and volumetric titrations. Every student standardized an NaOH solution gravimetrically and then analyzed a specific unknown using the gravimetric titration procedure. Three to five individual determinations were performed
by each student during the standardization and analysis procedures. The students were then given a different set of individual unknown KHP samples and asked to identify the weight percent of their unknown using volumetric titrations. In order to ensure full attentiveness to each experiment, the students were graded based on their accuracy and precision for each method.

In order to determine the differences in accuracy and precision between each method, the standard deviations of each student using each method were averaged and then statistically compared. It is important to note that the precision for a given method was quantified using the composite standard deviation of the individual students’ standard deviations. Accuracy was quantified using the absolute error of each student’s experimental weight percent KHP determination relative to the accepted value for each unknown. In order to reject the null hypothesis stating that each titration method would produce the same results, both the F-test and the T-test were performed. The F-test was used to determine if both the standard deviations for the volumetric and gravimetric titration methods were significantly different. The standard deviations determined by each student were averaged for both methods and used in an Excel program.

**Table 4. F-Test Results**

<table>
<thead>
<tr>
<th>P-Value</th>
<th>Standard Deviation</th>
<th>Absolute Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.11x10^{-6}</td>
<td>1.44x10^{-5}</td>
</tr>
</tbody>
</table>

The results presented in Table 4 show that the standard deviation and the relative error are significantly different for each method’s accuracy and precision. The P-value for each F-test indicated that the two methods had significantly different variances for both
precision and absolute error. The variances associated with the accuracy and precision of
the volumetric data is significantly larger than those of the gravimetric data.

The second statistical test performed on this set of data was the T-test. The results
of the F-test indicated that the T-test with unequal variances should be performed. The T-
test is used to show statistically whether two sets of reproducible data give the same or
different results. The average standard deviations for both precision and accuracy from
each student were determined using Microsoft Excel. The results are shown in Table 5
for precision and Table 6 for accuracy.

Table 5 and Table 6 confirm that gravimetric titrations give more accurate and
precise results. The absolute error in the determination of weight percent KHP by the
volumetric titrations was 0.652%, which was significantly higher than the absolute error
of 0.290% in the gravimetric titrations. Similarly, the average standard deviation
determined by the students for volumetric titrations was 0.447%, while that for the
gravimetric titrations was 0.185%.

The T-test also confirms that the null hypothesis can be rejected for both precision
and accuracy for each titration method. Comparing the mean values of precision for both
volumetric and gravimetric titrations, the reproducibility of results is worse for
volumetric titrations than it is for gravimetric titrations. Because the P-value associated
with the comparison of precision was 0.0473, the results are considered to be statistically
significant at a confidence level of 95.3%. For the comparison of accuracy, the P-value
was 0.0148, and the results are considered to be statistically significant with a confidence
level of 98.5%. It is clear from the statistical analysis that gravimetric titrations are
superior to volumetric titrations with respect to both accuracy and precision.
In a survey of the Quantitative Analysis students conducted after completing all of the analyses, there was a strong consensus that the gravimetric titrations were easier to perform than the volumetric titrations. The students were especially frustrated during the volumetric titrations with the control of the buret stopcock. Some had problems with leakage around the stopcock, while others had trouble reproducibly dispensing small amounts of titrant and controlling partial drops. The majority of the class also found that it was easier to get better results at a faster pace with the volumetric titrations. However, some students preferred the volumetric titrations since they were more comfortable using the volumetric burets and they felt it took less time to complete the process. The problems the students found with the gravimetric titrations were the leakage of drops from the tip of the gravimetric burets and the time-consuming process of waiting to use the analytical balances. The class came up with solutions to each problem associated with the gravimetric titrations; one solution being to provide caps for the tips of the gravimetric burets, thus decreasing the possibility of leakage. The other solution was to have the analytical balances closer to each student, thus eliminating the waiting process in order to use the balance.
Table 5. Precision T-Test

<table>
<thead>
<tr>
<th></th>
<th>Volumetric</th>
<th>Gravimetric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Standard Deviation of Raw Results</td>
<td>0.447</td>
<td>0.185</td>
</tr>
<tr>
<td>Standard Deviation of Individual Standard Deviations</td>
<td>0.586</td>
<td>0.218</td>
</tr>
<tr>
<td>Observations</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>P Value</td>
<td>0.0473</td>
<td></td>
</tr>
<tr>
<td>Confidence Level</td>
<td>95.3%</td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Accuracy T-Test

<table>
<thead>
<tr>
<th></th>
<th>Volumetric</th>
<th>Gravimetric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Absolute Error</td>
<td>0.652</td>
<td>0.290</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.625</td>
<td>0.247</td>
</tr>
<tr>
<td>Observations</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>P-Value</td>
<td>0.0148</td>
<td></td>
</tr>
<tr>
<td>Confidence Level</td>
<td>98.5%</td>
<td></td>
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</tbody>
</table>
References


