GRAVIMETRIC TITRATION – A LOW COST, HIGH PRECISION ALTERNATIVE TO VOLUMETRIC TITRATION

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Received 25/8/2016, Peer reviewed 10/12/2016, Accepted for publication 25/12/2016

ABSTRACT

In factories and in laboratories nowadays titrimetry is performed predominantly with the use of burets. In Vietnam there is almost no textbook and laboratory exercise manual of analytical chemistry mentioning about using electronic balance in titrations and comparing analytical characteristics of this technique with the traditional one using of buret. This work compares the two techniques using technical electronic balance and using buret when paralelly titrating a permanganate solution by a Mohr salt solution. Experimental results show that titration with a two-placed electronic balance yielded similar accuracy but better precision in shorter time, compared to using a buret. Using electronic balance also possesses several other advantages, such as low cost, safety, high mobility and ease of automation.

Keywords: *Electronic balance; buret; accuracy; precision; cost.*

TÓM TẮT

Hiện nay trong các nhà máy và trong phòng thí nghiệm, phương pháp chuẩn độ được thực hiện chủ yếu bằng buret. Tại Việt Nam chưa có sách giáo khoa hóa phân tích nào đề cập đến việc dùng cân kỹ thuật điện tử để chuẩn độ, cũng như so sánh các khả năng phân tích của kỹ thuật này với việc dùng buret truyền thống. Nghiên cứu này so sánh hai kỹ thuật dùng buret và dùng cân kỹ thuật khi được thực hiện song song cho phép chuẩn độ permanganat bằng muối Mohr. Kết quả thực nghiệm cho thấy kỹ thuật chuẩn độ dùng cân kỹ thuật hai số lẻ cho kết quả với độ đúng tương đương, độ chụm cao hơn, thời gian phân tích ngắn hơn so với dùng buret. Việc sử dụng cân điện tử còn có các ưu điểm khác như chi phí thấp, an toàn hơn, linh động hơn và dễ tự động hóa hơn so với kỹ thuật chuẩn độ dùng buret.

Từ khóa: *Cân điện tử; buret; độ đúng; độ chính xác; chi phí.*

1. INTRODUCTION

In analytical chemistry there are three types of quantitative titration: volumetric, gravimetric and coulometric [1]. In gravimetric or weight titration the amount of solution added to complete the reaction is measured by mass (using a balance), while in volumetric titration, the volume of titrant is measured traditionally by a buret. With a modern digital 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 [2, 3]. Moreover, reproducibility can even be much better although this does require a higher-precision balance, more time and more effort.

In a gravimetric titration, the titrating solution is contained in and dispensed from a gravimetric buret, which can be a modified syringe [4], or a small polymer drop-dispensing squeeze-bottle, fitted with either a glass or a polymer capillary tip [5] or just a plastic bottle with a dropping pipet [2]. These have been found to be very satisfactory gravimetric burets for student use; they are inexpensive, durable and easily modified to fit the requirements of gravimetric titrations.

The drop size from the gravimetric buret and the balance precision together determine the precision of the method. Guenther described a super-high-precision gravimetric titration method adopted by the U. S. National Bureau of Standards (NBS), where the result was reproducible to 1 part in 10,000 [6]. Butler and Swift described a high-precision gravimetric titration method for undergraduate university students, where the results were reproducible to 1 part in 1,000 (compared to 3 parts in 1,000 with a volumetric buret) [5]. This was achieved by modifying a 60 mL polymer wash-bottle capillary tip to deliver smaller drops.

McMills achieved a 0.34% relative standard deviation using a mass buret setup including a small plastic container with a short-stem glass dropping pipet [2]. However, the fragility and sharpness of the pipet's tip posed a safety hazard in the laboratory. In this work the authors report an all-plastic setup for mass titration with precision and accuracy comparable with that of volumetric titration.

2. MATERIALS AND METHODS

2.1 Materials

Unmodified 60 mL polymer drop-dispensing squeeze bottles were used as gravimetric burets. The glass reaction flask was replaced with a polyethylene cup. The hydrophobic character of this material reduced adhesion of reaction mixture with the wall while being swirled, thus made it easier to detect and rinse the adhered drops back to the reaction mixture near the endpoint. A MH-200 pocket top-load two-place digital balance (200g/0.01g) with auto-calibration function was purchased online (https://goo.gl/ezveJ0) and used to perform weight titrations.

2.2 Methods

In his work, Ramette introduced the concentration unit *molamity* as moles of solute per kilogram of solution [7]. This allows simple conversion to moles of titrant by multiplying molamity by the dispensed solution's mass. In this paper, the authors used *equivalent molamity* as moles of equivalents of solute per kilogram of solution. Permanganate method was used to evaluate precision, accuracy and convenience of gravimetric technique of titration. Concentration of a $KMnO_4$ solution was determined by a Mohr salt $(NH_4)_2Fe(SO_4)_2.6H_2O$ solution as primary standard with both volumetric and gravimetric techniques. In a typical gravimetric titration, about 10 g of Mohr salt solution (C_N = 0,09443N; eq. molamity = 0,09093 mol eq./kg) and 10 g of 20% H_2SO_4 solution were transferred to a plastic cup. The cup was then weighted before titration. $KMnO_4$ solution (C_N= 0,2048 N; eq. molamity = 0.2051 mol eq./kg) was added to the cup by a gravimetric buret until a permanent pale pink color remains for at least

30 seconds. The mass of dispensed titrant can be identified by calculating the difference in weight of the buret or of the reaction cup. Concentration of the $KMnO_4$ solution was calculated by the following formula:

$$C_{KMnO_4} = \frac{C_{Mohr} \cdot m_{Mohr.sol}}{m_{KMnO_4.sol}}$$

Where: C_{KMnO_4} and C_{Mohr} - equivalent *molamity* of $KMnO_4$ and $FeSO_4$, respectively, in 1 kg of solution; $m_{KMnO_4.sol}$ and $m_{Mohr.sol}$ - masses of added $KMnO_4$ solution and Mohr salt solution, respectively.

3. RESULTS AND DISCUSSIONS

3.1 Precision and accuracy of gravimetric titration

Precision of gravimetric titration technique was evaluated by the percent relative standard deviation (%RSD) of the calculated values of $KMnO_4$ concentration [8]. The results showed that for N = 7 replicate analyses, when the average mass of used titrant was 2.56 g, the %RSD was 1.9%. When the mass of dispensed titrant increased to 4.63 g, the %RSD was improved to 0.68%. The range of these %RSD values is acceptable for most of analytical works in industries and practical laboratories. %RSD in the latter case was lower than that in volumetric titration with the same solutions (0.77%). This finding was in agreement with the works of McMills and Thompson, who also found gravimetric technique improved precision of titration [2, 3]. Even in pharmaceutical industry, the recommended %RSD for precision is 1% for drug substances and drug product, 2% for bulk drugs and finished products [9], so the precision of gravimetric titration is acceptable for practical uses.

Normally the precision of titrations can be improved by increasing the volume or mass of the titrated sample. Another way to improve precision of gravimetric titration is decreasing the size of titrant drops from the gravimetric buret by modifying the plastic tip of the buret [5] or replacing it with a glass capillary tip.

To evaluate the accuracy of gravimetric titration technique, concentrations of the permanganate solution identified by the gravimetric (0.211±0.002 mol eq./kg) and volumetric titrations (0.204±0.002 N) were compared with the “real” concentration (0.2048 N; 0.2091 mol eq./kg) calculated from the masses of solid $KMnO_4$ and water used to prepare the solution. In both cases, the true value of $KMnO_4$ concentration is within the 95% confidence intervals of the mean in both titration techniques. It means that results generated from gravimetric titration are acceptable in terms of accuracy and comparable with that of volumetric titration.

3.2 Convenience and economic considerations

Gravimetric titration is much cheaper.

In this work, a digital two-place balance and a plastic squeeze-bottle (totally about $4) satisfactorily replaced a volumetric buret (about $48) with better precision and comparable accuracy. And compared to classic volumetric burets, plastic gravimetric buret cannot be broken. We can see that a setup for gravimetric titration is more than 10 times cheaper than the volumetric counterpart. This is especially meaningful for schools and universities in developing countries like Vietnam.

For repeated gravimetric titrations there is no need to initially fill and finally empty the burets for each day’s experiments, so the amount of titrating reagent solution required is much reduced. The incidence of spills will also be lessened.

Gravimetric titration is safer.

Volumetric titration contained more hazard than gravimetric titration because it uses glassware, which is easily to be broken. In many cases in freshman chemistry laboratory some students need to climb a stool to read the meniscus in a buret, and that can lead to accidents. This risk is eliminated with a digital balance and a plastic bottle.

Gravimetric titration is more convenient.

Calibration was faster and easier. With only one weight of 200.00 g, a digital balance can be automatically calibrated in less than 30 seconds, while calibrating a buret requires much more time and work. In gravimetric titration temperature corrections are unnecessary because the mass (weight) molar concentration does not change with temperature, in contrast to the volume molar concentration. This advantage was particularly important in non-aqueous titrations because of the high coefficients of expansion of most organic liquids (about 10 times that of water) [1].

A gravimetric kit (a pocket digital balance, plastic buret and cups) is simple and portable, so it can be used right at a production line, or in nature, where a volumetric buret with a heavy clamp could hardly be useful.

In volumetric titrations a pipet must be used to dispense an exact volume of the solution that need to be titrated. This is unnecessary in gravimetric titration, where this solution can be dispensed directly from its container, and its amount is registered by the digital balance.

The procedure of gravimetric titration is faster.

Rinsing the buret, pipet and flask before and after titrations in volumetric technique require more time. The reasons for that are: water wets glassware, not plastics; handling a squeeze-bottle while rinsing is easier than a long glass buret; glass pipet is not needed in gravimetric titration.

The endpoint control in gravimetric titration is better. For those, who do not frequently practicing volumetric titration, it is hard and time-consuming to titrate when the endpoint is coming because the procedure drop-stop-swirl requires patience and skill. 50/50 second-year students of HCMUTE after a head-to-head experiment confirmed that the last drops of titrant from a squeeze-bottle buret can be dispensed in a highly more controllable manner and without any stress. In average a student needed less than 2 minutes to complete one titration using gravimetric technique but more than 4 minutes using volumetric buret.

Gravimetric titrations are more easily automated than volumetric titrations [1, 10].

Gravimetric titrations require less skill than volumetric counterpart. So we expect that it would be accepted and applied widely in industries and laboratories.

Disadvantages of gravimetric titration. The mass reading is affected by the air movement cause by wind or people movement, especially for high-precision titrations with three- or four-place balances. However, this disadvantage can be easily eliminated with a plastic cap initially attached by the balance manufacturer (https://goo.gl/QegNjd).

In some cases when the titrant can react with the plastic wall of the gravimetric buret, glass bottle or beaker and pipet are required to work with it.

4. CONCLUSION

From the above comparisons and considerations, we can see that the emergence of inexpensive electronic balances have indeed brought glass burets one step closer to being removed from laboratory service. It is suggested to encourage chemistry teachers in schools and in universities courses to accept this gravimetric technique and construct laboratory exercises to introduce mass-based titrations to next generations of chemists and technicians whose work is relating to titrations.

REFERENCES

[1] Skoog, D.A., et al., *Fundamentals of analytical chemistry*. 2013: Nelson Education.
[2] McMills, L., F. Nyasulu, and R. Barlag, *Comparing mass and volumetric titrations in the general chemistry laboratory.* Journal of Chemical Education, 2012. 89(7): p. 958-959.
[3] Thompson, J.E. and L. Brode, *My Dear Buret, Your Time Has Indeed Come!* J. Chem. Educ, 2016.
[4] Thoburn, J.M., *Weight titrations revived.* J. Chem. Educ, 1959. 36(12): p. 616.
[5] Butler, E.A. and E.H. Swift, *Gravimetric titrimetry. A neglected technique.* J. Chem. Educ, 1972. 49(6): p. 425.
[6] Guenther, W., *Supertitrations: High-precision methods.* J. Chem. Educ, 1988. 65(12): p. 1097.
[7] Ramette, R.W., *Gravimetric Titrations: In Support of Weight Titration Techniques.* J. Chem. Educ, 2004. 81(12): p. 1715.
[8] IUPAC. *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"). Blackwell Scientific Publications, Oxford (1997).
[9] U.S. FDA, *Guidance for Industry: Analytical Procedures and Methods Validation: Chemistry, Manufacturing and Controls Documentation*, August 2000.
[10] Luft, L., *Automated gravimetric titrations.* Talanta, 1980. 27(2): p. 221-222.

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