

Weight Titrations: A Forgotten Art?

A.J.C.L. HOGARTH
Department 417
Ross Laboratories
625 Cleveland Avenue
Columbus, Ohio 43216

A Brief History of Weight Titrimetry

Weight titrimetry has been a part of analytical chemistry for many years; it certainly predates volumetric analysis by at least half-a-century if not longer. The clear reason for this state of affairs is that while weighing was a well-developed method of measurement, the standard glassware needed for volumetric analysis was not available, at least not until the beginning of the nineteenth century when such French chemists as Descroizilles started to develop it.

One of the first recorded analyses by what is clearly weight titrimetry was by Guillaume Homberg in 1699 (7). He titrated potash with nitric acid by weighing the former in small portions into the latter until reaction ceased. The end-point of this reaction would certainly have been cessation of effervescence but Homberg did not mention this in his paper. Some thirty years later in 1729 Claude Geoffroy read a paper to the French Academy concerning his researches with vinegar: he added weighed quantities of dry potassium carbonate to vinegar until the bubbling stopped, a clear indication of the reaction end-point (7).

Other notable workers were Francis Home in 1756 who, in his book "Experiments on Bleaching", described the analysis of various liquors and solutions by weighing; William Lewis, in 1767, in a monograph entitled "Experiments and Observations on American Potashes with an Easy Way of Determining Their Respective Qualities" described various methods of titration based upon weighing; Carl Friedrich Wenzel in 1777 wrote a book dealing with "titrimetric synthesis" in which he used weight titration as a method of investigating the stoichiometry of certain reactions; and Louis Bernard Guyton de Morveau who, in 1793, used the method to investigate the titration of carbonate solutions with lead solution.

Evidently the method has quite a distinguished history which was submerged almost completely by the advent of volumetric analysis. This does not mean, however, that the method was totally lost because periodically papers have appeared in the literature dealing with analyses using weight titrimetry. For example Washburn (9) used the method at the turn of the century for the determination of arsenious acid iodometrically. His apparatus was a little complicated but the results he obtained showed excellent precision, about 0.1ppt.

Several designs for apparatus have appeared in the literature, the most common one being that of Friedman and LaMer (3). This is shown in Figure 1 and is essentially a modified separating funnel with side hooks to support it in a balance chamber, a drawn tip for drop delivery, and a ground glass cap for the tip to prevent loss by evaporation. A weight buret constructed from a polythene wash bottle was successfully used by Seils, Meyer and Larsen for the determination of plutonium (VI) with iron (II) (8). In 1969 Davenport published a short paper dealing with the use of plastic baby-bottles in general chemistry laboratories for several experiments (2).

More recently, however, Kratochvil has revived a little interest in the method as a convenient way of conducting titrations with non-aqueous solvents (6). He has extended the method for use with a modern top-loading balance attached to a small computer (5). This arrangement has many possibilities largely because of the flexibility of the com-

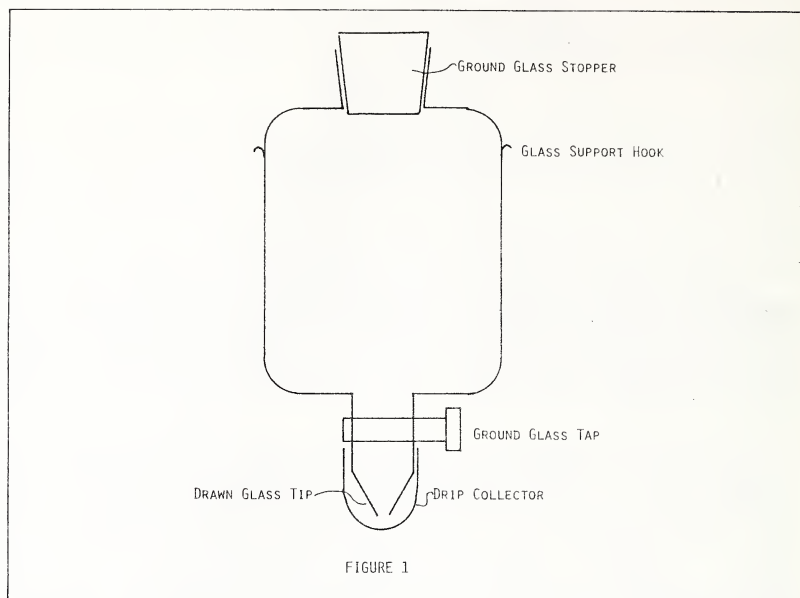


FIGURE 1. Classical weight burette.

puter, and will allow the simultaneous titration and plotting of a variety of titration curves.

The object of this short paper is to show the value and utility of this technique for teaching some of the principles of analysis, stoichiometry and quantitative method as applied to simple chemical systems. The experiments that will be described, although originally devised for a freshman general chemistry class, could, with little modification, be used in high schools or introductory analytical chemistry classes.

The Advantages and Uses of Weight Titration

- 1) The apparatus used is less expensive and often more durable than that for volumetric analysis.
- 2) A weight titration may be more precise, and can often be made more so, whereas there is a limit to the corresponding volumetric titration (1).
- 3) Changes in calibration of glassware due to fluctuations in temperature are non-existent.
- 4) Syringes or small plastic dispensing bottles are easier to fill and clean than burets and pipets, and they do not break as readily.
- 5) Syringes and small plastic dispensing bottles require far less practice to use effectively (4). Burets and pipets often require a great deal of effort for correct use.
- 6) There is no confusion between 'TO CONTAIN' and 'TO DELIVER' notation, i.e. how long to allow the apparatus to drain?
- 7) There are savings in time for titration as well as in the quantities of reagents used.
- 8) Titration can be very rapid, e.g. twelve titrations in one hour, and this includes all the weighings!
- 9) Automation of the titration is possible with the use of a modern top-loading balance.

- 10) Titration is possible with volatile or classical toxic reagents with convenience and relative safety. For example:
- Arsenic standardization with oxidizing agents.
 - Titration with expensive reagents, e.g. silver nitrate.
 - Titration of plutonium. The apparatus is so inexpensive that it may be disposed of immediately after use.
 - Titration with reagents contained in volatile or non-aqueous solvents, e.g. caffeine using perchloric acid in glacial acetic acid, or the Karl Fischer titration for water.
 - Titration with somewhat unstable reagents, e.g. titanous chloride for the azo group in certain dyes.

The Titration Procedure and Apparatus

The procedure adopted for weight titrations is quite a simple one and is as follows:

- Solutions are prepared by dissolving a weighed quantity of analyte or titrant in a weighed amount of solvent. Usually both the solvent and solute are weighed into a simple plastic dispensing device (Figure 2a). Another way of doing it is to weigh both solvent and solute into a stock vessel for mixing and then dispense from a syringe (Figure 2b). Syringes present a problem in that they frequently come with a needle, and this does occasionally result in disposal difficulties.

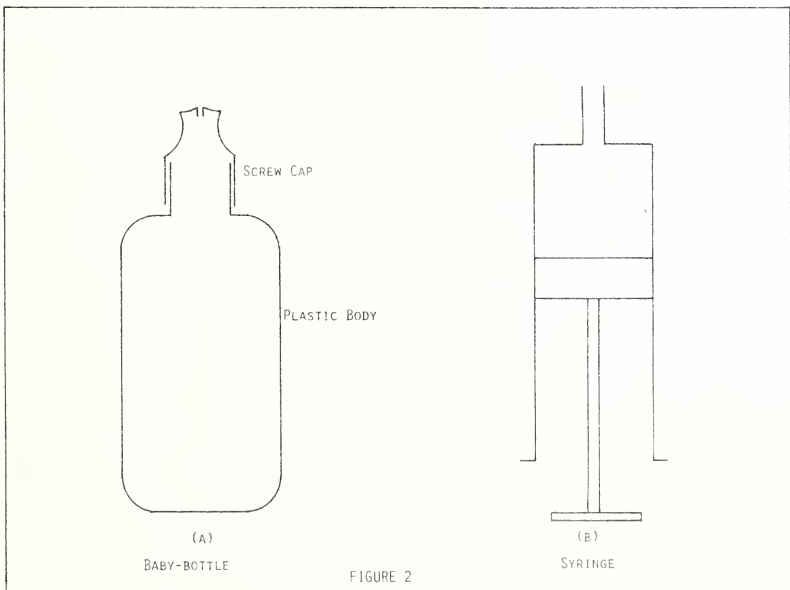


FIGURE 2. Commonly available devices for weight burettes.

- Both the analyte and titrant are weighed for the purposes of the titration. Either may be a solid but one, at least, should be a solution for the sake of convenience. If the titrant is a solid it may be dispensed from a carefully held bottle, or it may be titrated with the analyte.

c) A suitable end-point detector should be chosen: visual indicators are usually very convenient, e.g. colorimetric or cessation of gas evolution. The experiment could be made more interesting for advanced students by using an instrumental end-point detector, e.g. pH-electrode, thermometer, etc.

Comparing Weight Titrimetry to Volumetric Titrimetry

A) Titration of Solid Potassium Hydrogen Phthalate (KHP) with Sodium Hydroxide

A quantity of KHP is accurately weighed (ca. 0.3g-0.5g) into a small flask and dissolved in about 25ml of distilled water. Two drops of phenolphthalein indicator are added and the solution is titrated to a pink end-point with sodium hydroxide solution.

a) Results for Volumetric Titration

Nine titrations gave a value for the ratio (volume of sodium hydroxide solution/weight of solid KHP) of (31.67 ± 0.14) ml of solution/g of KHP with a precision of 3.6ppt. Taking one significant figure less in both the weighings and volume readings gave (31.69 ± 0.18) ml of solution/g of KHP with a precision of 4.2ppt.

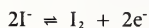
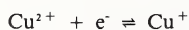
b) Results for Weight Titration

Nine titrations gave a value for the ratio (weight of sodium hydroxide solution/weight of solid KHP) of (31.83 ± 0.10) g of solution/g of KHP with a precision of 1.9ppt. Taking one significant figure less in the weighings gave a value of (31.82 ± 0.10) g of solution/g of KHP with a precision of 2.2ppt.

Clearly there is little to distinguish between the two sets of titrations from the point of view of precision. If, however, they are compared with regard to the time spent on the experimental work, then true differences show. The weight titration was performed by a person with little or no training in chemistry and taking half-an-hour, and the volumetric experiment was performed by a person of experience and took an hour. Evidently more experimental work could be accomplished in the ever-shortening practical periods attached to chemistry courses!

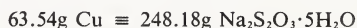
B) Percentage of Copper in a Soluble Copper Salt

This determination was based upon the classical redox experiment:



An amount of the copper salt, about 5g, was weighed accurately and dissolved in a weighed amount of water, about 100g, and some sodium thiosulfate, about 7g, were weighed accurately and dissolved in a weighed amount of water, again about 100g. Portions of the copper solution were weighed, about 6-10g, a spatulaful of solid potassium iodide added, and then the released iodine was titrated with the sodium thiosulfate solution to a starch end-point. The titrant was weighed before and after the titration.

From the reaction equations above it can be seen that



Therefore it follows that if, for example, the solutions contained 5.478g/100g of solution of copper salt and 7.808g/100g of solution of sodium thiosulfate, and W_C and W_N are the weights used of these solutions respectively, then:

$$\% \text{Cu} = (63.54/248.18) \times (7.808/100) \times (100/5.478) \times 100 \times (W_N/W_C)$$

This experiment was performed using the solutions prepared with the concentrations as

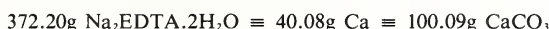
above, and eight titrations yielded a mean value of $(25.54 \pm 0.20)\%$ with a precision of 7.0ppt, comparing very well with a precision of about 12-15ppt when the experiment was performed volumetrically by a group of students.

Again the speed of this method showed well taking again about half the time that would normally be allocated to such an experiment. The time saved in this case was used by asking the students to develop a titration for the determination of sulfate but using a slightly different end-point indicator.

Determination of the Composition of Dolomite

This experiment is a simple one based upon the reaction of the material ethylenediaminetetra-acetic acid (EDTA) with calcium. EDTA is capable of reacting on a 1:1 molar basis with at least 70% of the metals of the Periodic Table.

The sample of dolomite, about 0.1-0.4g, is weighed accurately and dissolved in the minimum amount of 2M hydrochloric acid with gentle heating. The solution is then made basic, about pH = 10-11, with 2M sodium hydroxide. The pH may be tested using universal indicator paper. Add murexide indicator to the solution and titrate immediately from light pink to purple. Note the weight of titrant used. In this case it might be appropriate to experiment first to see if the 'before' and 'after' colors of the indicator.



Let W_S = weight of sample (g)

W_C = weight of calcium carbonate (g)

W_M = weight of magnesium carbonate (g)

W = weight of titrant (g)

Q = concentration of titrant in g EDTA/100g of solution

Therefore: $372.20\text{g Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O} \equiv 100.09\text{g CaCO}_3$

$$W \times Q \equiv W_C$$

thus $W_C = (100.09/372.20) \times W \times Q$

and $W_M = W_S - W_C$

For a certain experiment with $Q = 1.827\text{g}/100\text{g}$

W_S (g)	W (g)	W_C (g)	W_M (g)
0.104	11.80	0.058	0.046
0.268	29.31	0.144	0.124
0.193	21.57	0.106	0.087
0.397	42.94	0.211	0.186

Based upon these results the average composition of dolomite is:



From this information it is clear that the composition of dolomite is:



Again this experiment is short enough such that a class of fifteen equipped with a single top-loading balance with a capacity of 160g reading to two or three decimal places can easily finish the experiment in two hours.

Conclusion

All the experiments described take less time than their volumetric counterparts, thus allowing the student to investigate additional problems set by the instructor. These pro-

blems may be given to the class en masse on a sheet of paper, or they can take the form of personal suggestions made by the instructor to the student verbally. In either case it is important that the student come to grips with chemical problems experimentally.

Extra questions asked of the students can also be tailored to the abilities of individuals at the discretion of the instructor. Some students work faster than others and it is necessary to hold their interest in some fashion. Their particular questions could take the form of short literature projects based upon readings selected from the primary sources by the instructor which suggest further practical work. For the slower students the extra work may be identical to that of the faster students but should be presented a little more directly, and then reinforced by verbal comments by the instructor.

Finally, the experiments described in the previous section represent only a small number of those possible, and it would be quite possible to design ones for most purposes. For example, some laboratories lack the funds to give students a full practical course, and so experiments performed have to be inexpensive. For example an experiment using baking soda and white vinegar can be just as illustrative as one using sodium hydroxide and potassium hydrogen phthalate.

Acknowledgments

The author wishes to thank several classes of students who painfully ran the gamut of the experiments and, particularly, Renée Doll and Susan Cassidy who were patient enough to test the method against volumetric analysis for the acid-base titration.

Literature Cited

1. Bishop, E. 1959. High Precision Titrimetry. II. A System of Weight Titrimetric Analysis Using Arbitrary Standards. *Anal. Chim. Acta.* 20:405-412.
2. Davenport, D.A. 1969. Baby-Bottles and Elementary Chemistry. *J. Chem. Ed.* 50:629-630.
3. Friedman, H.B. and LaMer, V.K. 1930. An Improved Weight Buret. *Ind. Eng. Chem. (Anal. Ed.)*. 2:54.
4. Gaddis, S. 1959. Titration Without Burets. *J. Chem. Ed.* 36:290.
5. Guevremont, R. and Kratochvil, B. 1978. Automatic Gravimetric Titration System. *Anal. Chem.* 50:1945-1948.
6. Kratochvil, B., Findlay, E.J. and Harris, W.E. 1973. A Nonaqueous Gravimetric Titration: Determination of 8-Hydroxyquinoline with p-Toluenesulfonic Acid in Acetonitrile. *J. Chem. Ed.* 50:629-630.
7. Madsen, E. Rancke. The Development of Titrimetric Analysis till 1806. 1958. G.E.C. Gad, Copenhagen.
8. Seils, C.A., Meyer, R.J. and Larsen, R.P. 1963. Amperometric Titration of Plutonium(VI) with Iron(II). *Anal. Chem.* 35:1673-1675.
9. Washburn, E.W. 1908. The Theory and Practice of Iodometric Determination of Arsenious Acid. *J. Am. Chem. Soc.* 30:31-46.