Near as makes no difference?

Volumetric analysis is one of the bedrocks of quantitative chemistry and remains an important technique for students of chemistry to master. In a school setting at least, it is synonymous with titration which in turn is a technique that has changed little in over a century. But are we, perhaps, focussing too much on the process and not enough on what we are trying to measure?

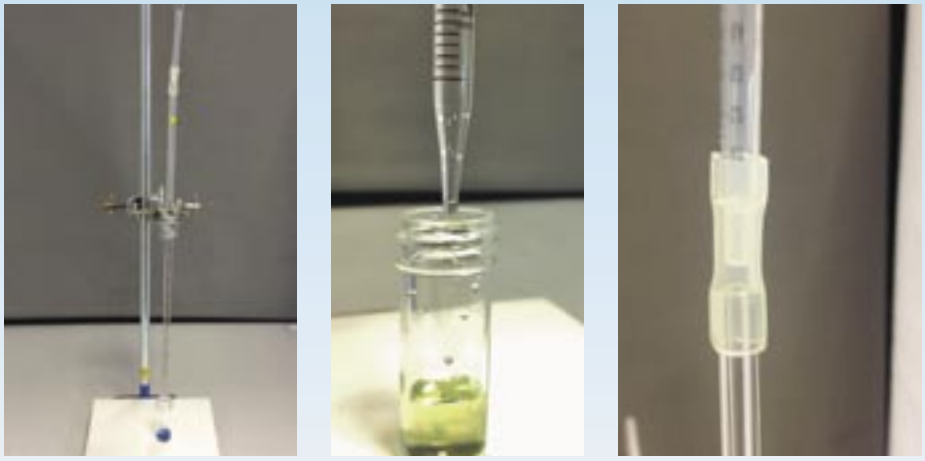

Figure 1 *- Microscale titration using a graduated pipette.*

The traditional titration is a good technique and an important one for students to master. It does, however, have a few drawbacks; burettes are relatively expensive and fragile and titrations use quite large quantities of solutions.

In this article, we are going to show a couple of alternatives to the traditional titration and evaluate their convenience and accuracy.

1) Microscale titration using a graduated pipette

This is simply a scaled down version of a 'normal' titration. A 1 cm^3 or 2 cm^3 pipette takes the place of the burette and the flask is replaced with a small vial or test tube.

A syringe is fixed to the top of the pipette by means of a short length of silicone tubing and this can be used to draw up the titrant into the barrel of the pipette. The syringe can then be used to dispense the titrant drop by drop by applying gentle pressure (Figure 1).

The method is simple and reliable and easy to master. It is also similar enough to a 'normal' titration to be familiar.

2) Microscale titration using a Pasteur pipette

In this case, the burette is replaced with a Pasteur pipette that dispenses the titrant drop by drop (Figure 2). A normal 1 cm^3 pipette will give on average 25 drops per cm^3, meaning each has a volume of 0.04 cm^3. Better results can be obtained by using fine tipped pipettes; these produce smaller drops, about 50 to the cm^3, giving each one a volume of about 0.02 cm^3.

It is possible to simply hold the pipette in your hand but there is a tendency to change the angle at which you are holding it and this can affect the size of the drops. A much better method, in many ways, is to hold the bulb of the pipette in a laboratory clamp. Turning the screw to tighten the jaws of the

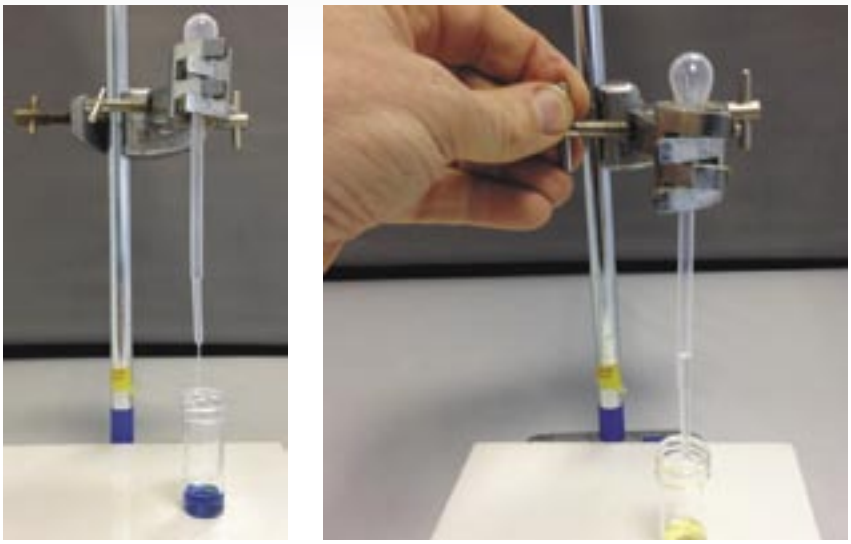

Figure 2 *- Microscale titration using a Pasteur pipette.*

Figure 3 *- Counting drops.*

clam slowly squeezes the bulb and expels the titrant slowly enough that you have a high level of control.

Unlike a burette, these pipettes have no scale on the barrel so we need to find other methods to determine the volume. There are two ways:

a) Counting drops

With a reasonable amount of care, the pipettes will dispense drops of a uniform size (0.04 or 0.02 cm^3). So a simple count of the number of drops can easily be converted into volume.

This is fine if your volume is relatively small compared to the drop size but if not you will end up having to count too high and will end up frustrated when you lose count. This problem can be avoided if you take an entirely different approach that might seem odd when talking about volumetric analysis …

b) Measuring the mass

Most aqueous solutions, unless they are quite concentrated, have a density very close to that of water. That makes it easy to simply take the density as 1 g/cm^3 and to measure the mass as a proxy for the volume.

The advantage of this approach is that it is much easier to measure mass accurately than volume. It is true that normal laboratory balances are quite expensive and so this would not solve the issue of expense associated with burettes but pocket 0.01 g balances can be bought for around £5.00 now and these, while not perhaps as robust as laboratory balances are, in our experience, just as accurate.

Accuracy

The important thing here is to find what is the limiting factor.

Reading accuracy

Burette - the limiting factor here is the accuracy with which it is possible to read the scale. Most burettes have markings every 0.1 cm^3. It is, with care, perhaps possible to read half graduations. If we assume so then that means we have an accuracy of 0.05 cm^3. In fact, the drop size from a burette is around 0.05 - 0.06 cm^3 so this is indeed the level of accuracy.

Pipette - the markings on a 1 cm^3 pipette are every 0.01 cm^3 and it is possible to read intermediate values as with a burette. However, the drops from pipettes have a volume of 0.04 cm^3 so this is the minimum level of accuracy.

Pasteur pipette - when dealing with drops from a pipette, the fact that a balance can measure to 0.01 cm^3 is neither here nor there as the minimum drop side is either 0.04 or 0.02 cm^3.

Error

The accuracy to which it is possible to take a reading is only part of the story though. The titre volume plays a part too.

If we take a standard titration as about 25 cm^3 then reading to 0.1 cm^3. This gives a theoretical accuracy of ± 0.4%.

For the microscale titrations, let us assume a titre of 1 cm^3. In this case, a drop size of 0.04 cm^3 gives an accuracy of ± 2% using fine-tipped pipettes. Increasing the volume to 2 cm^3 improves the accuracy to ± 1%.

This is not quite as good but certainly reasonably close.

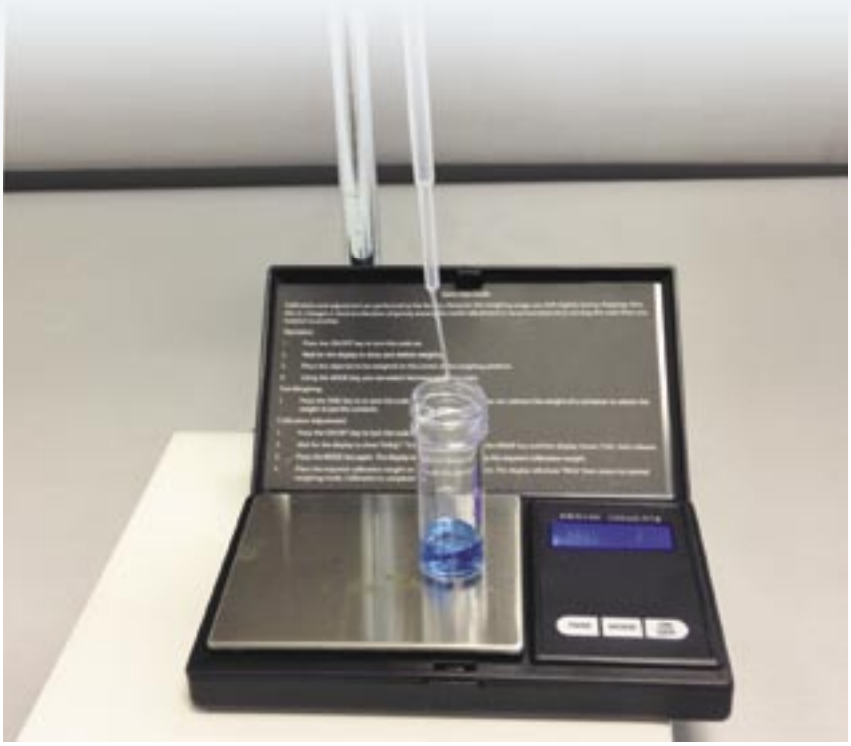

Figure 3 *- Measuring the mass.*

TITRATION 1 - conventional titration						
vol of alkali	[alkali]	moles	vol of acid		[acid]	
20	0.1	0.002	18.9		0.1058	**Molarity = 0.106**
20	0.1	0.002	18.9		0.1058	
20	0.1	0.002	18.8		0.1063	
TITRATION 2 - 1 cm³ pipette (with syringe adaptor)						
vol of alkali	[alkali]	moles	vol of acid		[acid]	
1	0.1	0.0001	0.96		0.1041	**Molarity = 0.104**
1	0.1	0.0001	0.95		0.1053	
1	0.1	0.0001	0.96		0.1042	
TITRATION 3 - 2 cm³ pipette (with syringe adaptor)						
vol of alkali	[alkali]	moles	vol of acid		[acid]	
2	0.1	0.0002	1.85		0.1081	**Molarity = 0.108**
2	0.1	0.0002	1.85		0.1081	
2	0.1	0.0002	1.87		0.1069	
TITRATION 4 - drops from 1 cm³ fine tip pipette by drops						
vol of alkali	[alkali]	moles	drops of acid	vol of acid	[acid]	
1	0.1	0.0001	50	0.96	0.1041	**Molarity = 0.103**
1	0.1	0.0001	51	0.98	0.1021	
1	0.1	0.0001	51	0.98	0.1021	
TITRATION 5 - drops from 1 cm³ fine tip pipette by mass						
mass of alkali	[alkali]	moles	mass of acid		[acid]	
0.97	0.1	0.000097	0.91		0.1066	**Molarity = 0.108**
0.99	0.1	0.000099	0.92		0.1076	
0.98	0.1	0.000098	0.90		0.1088	

Table 1 *- Series of titrations.*

How good is good enough?

When considering the accuracy of a technique, however, we need to consider how accurate we need to be in each case. If we needed to be as accurate as is possible in every case, we would make up every solution in volumetric flasks using a 3 (or more) place balance. While there are times when this level of care is absolutely required, there are plenty of occasions where it is not. So the question is, is the level of accuracy of these simpler techniques sufficient for general usage or not?

Let us look at a real life example. Table 1 shows some results of a series of titrations of 0.1 M sodium hydroxide with 0.1 M hydrochloric acid. Neither of these was standardised but that does not matter for the purposes of our calculations.

We have assumed that the molarity of the NaOH is exactly 0.1 M and have used the titre to calculate the concentration of the HCl solution (see Table 1).

Conclusions

As you can see from the data above. These simple methods can give pretty accurate results. A molarity of 0.104 or 0.107 compared to 0.106 is, in our view, certainly good enough. Even the least accurate method, counting the drops, gives 0.102 M which is fine for most purposes - in fact in most cases the accuracy with which the solutions are made up is likely to have a greater effect.

Where accuracy matters, in Advanced Higher projects for instance, then of course the standard method should be used. It is also important as a part of their preparation for exams that pupils are familiar with the apparatus and techniques of a classical titration.

However, where apparatus is in short supply or where expensive reagents are involved, in argentometric titrations for instance, the microscale approaches detailed above give perfectly adequate results and allow quantitative chemistry to be done much more easily and by every individual in the class rather than as part of a group.