Accuracy, Precision and Analytical Measurements

What are accuracy and precision?

Accuracy is how close a measurement is to its desired or theoretical value. For example, if we need to dispense 25.0 mL of dilute HCl, then dispensing 24.9 mL is more accurate then dispensing 25.7 mL. Accuracy usually is reported as a percent error

$$\% \text{ error} = \frac{\text{actual value} - \text{expected value}}{\text{expected value}} \times 100$$

which, for the two examples cited above, are $\frac{24.9-25.0}{25.0} \times 100 = -0.4\%$ and $\frac{25.7-25.0}{25.0} \times 100 = +2.8\%$. Note that an error that affects accuracy is either positive or negative.

Precision is the reproducibility of a set of measurements. Three identically prepared solutions with pH values of 6.76, 6.73, and 6.78, for example, are more precise than a duplicate set with pH values of 6.76, 6.54, and 6.92. Precision usually is reported as a standard deviation, s, which we define as

$$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n-1}}$$

where $\bar{x}$ is the average, or mean result, and x_i is one of the n different results. If you closely examine this equation you will see that a standard deviation essentially is the "average" deviation of the individual measurements from their mean value.[1] Note, as well, that squaring the term in the numerator guarantees that the standard deviation is always positive. As an example, the mean pH for the measurements 6.76, 6.73, and 6.78 is

$$\frac{6.76 + 6.73 + 6.78}{3} = 6.757$$

and the standard deviation is

$$s = \sqrt{\frac{(6.76 - 6.757)^2 + (6.73 - 6.757)^2 + (6.78 - 6.757)^2}{3-1}} = 0.0252$$

Alternatively, we can express the standard deviation as the percent relative standard deviation, s_r, or rsd

$$s_r = \frac{s}{\bar{x}} \times 100$$

For the example above, the relative standard deviation is $\frac{0.0252}{6.757} \times 100 = 0.373\%$.[2]

[1]Note that the standard deviation is not a true average because we divide the numerator by $n-1$ instead of by n. The reason for this is not important to us at this time.

[2]Although you can calculate the mean and the standard deviation by hand, it is inconvenient to do so for a large data set. All scientific calculators and spreadsheets have the ability to calculate the mean and the standard deviation; learn how to do so with your calculator and/or favorite spreadsheet.

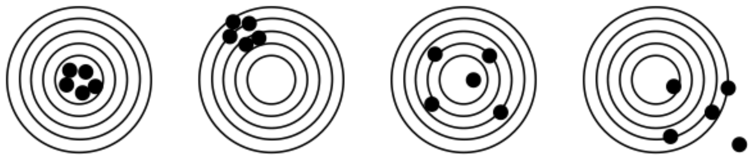

Figure 1: Clusters of five rifle shots illustrating the difference between accuracy and precision.

Is a pH of 6.76 both more accurate and more precise than a pH of 6.8?

Good question. It is tempting to say that a pH of 6.76 is more accurate than a pH of 6.8 because it contains more significant figures, but this is not necessarily correct. In fact, if the instrument used to measure the pH is not calibrated, then neither pH reading is accurate.

Regardless of its accuracy, we can say that a pH of 6.76 is known more precisely to us than a pH of 6.8 because the absolute uncertainty for the first measurement is ± 0.01 while that for second is ± 0.1.[3] If the pH meter is calibrated properly, then a more precise measurement can lead to a smaller percentage error and, consequently, to better accuracy.

If a measurement is accurate, must it also be precise?

Interestingly, the answer to this question is no. As we see in Figure 1, there are four possible combinations of accuracy and precision.

The target at the far left shows both accuracy and precision as the shots are clustered together (they are precise) in the target's center-most ring (they are accurate). The next example shows results that are precise, due to a tight clustering of the shots, but inaccurate because they are at the target's outer edge instead of its center. The third example is considered accurate because the five shots cluster around the target's center, but they are not precise because the individual shots are quite far apart from each other. The final example shows a dispersion of shots that is both inaccurate and imprecise. Note that the average for a set of measurements may be accurate even if the individual measurements deviate significantly from the desired or theoretical value.

What factors affect accuracy and precision?

Three main factors affect the accuracy and the precision of a measurement: the quality of the equipment we use to make the measurement, our ability to calibrate the equipment, and our skill using the equipment. These factors are considered further in this section.

We cannot make an accurate measurement if our equipment is not calibrated properly. To calibrate equipment we analyze a system where the response is known to us and either adjust the equipment to give that response or determine the mathematical relationship between the measured result and its known value. The two examples of accurate target shooting in Figure 1—the target on the far left and the target second from the right—require that you calibrate the rifle's scope so that an accurate result is possible. In addition, the potential accuracy of any individual measurement is greater with better quality equipment or instrumentation; the better the scope, the closer each shot is to the target's center.

Precision, on the other hand, is influenced by both the quality of the equipment and the skill of the person using it. The importance of the user's skill is obvious; when shooting a rifle, for example, you must have a steady hand to achieve a tight, precise pattern of shots. Although less obvious, the quality of the equipment

[3] We also can think about this in terms of relative uncertainty where 6.76 has a relative uncertainty of 1 part in 676, or 0.148%, and where 6.8 has a relative uncertainty of 1 part in 68, or 1.5%.

is equally important. The smooth bored muskets used during the Revolutionary War, for example, produced less precise shot patterns than those of a modern rifle because they lacked grooved bores.

Shouldn't I always strive for the best possible accuracy and precision?

Surprisingly, the answer to this question is a resounding NO. Improving accuracy and precision almost always comes at the expense of time and money. Calibrating an instrument, for example, takes time and the better the quality of the instrument, the more the instrument costs and the less likely it is to be freely available for your use because fewer units are available. You can save a lot of time and aggravation in lab if you learn to make the most accurate and precise measurement only when it is absolutely necessary.

So, how do I decide whether a measurement needs to be accurate or precise?

The simplest answer is this: if the result of the measurement is used in a calculation, then you should try to make the measurement with a suitable level of accuracy and precision. Note the use of the adjective suitable. If you must know the final result to within $\pm 1\%$, then the requirements you place on your individual measurements are more stringent than if your final accuracy must be within $\pm 10\%$. The same observation holds true for precision.

A useful method to determine how accurate or precise to make a measurement is to use significant figures as a guide. For example, if a procedure calls for a 1-L solution of 0.1 M NaCl, then you do not need an accurate or a precise measurement of the mass of NaCl or the volume of water. You can simply measure approximately 5.8 g of NaCl and dissolve it in a 1-L reagent bottle and know the molarity is 0.1 to within one significant figure. Or, if a procedure requires that you add approximately 0.01 g of a reagent to each sample, weigh out the first portion to judge the amount and simply add a similar portion to the remaining samples; there is no need to weigh out and record each addition. On the other hand, if a procedure calls for a 1.000-L of a 0.1000 M solution of NaCl, then it is necessary to weigh out 5.844 g of NaCl and to use a 1-L volumetric flask to prepare the solution.

When you use significant figures as a guide to determining a measurement's appropriate accuracy and precision, be sure to consider how the value is used in a calculation. If a procedure calls for a solution of NaCl with a nominal concentration of 0.1 M but the exact concentration is essential when you analyze your results, then you must obtain an accurate and precise mass of NaCl and dilute to volume in a volumetric flask; the exact concentration is then calculated. Alternatively, you can prepare the solution without regard to accuracy and precision and determine the concentration of NaCl experimentally, a process we call standardization. Let the procedure from which you are working guide in you making such decisions.