Handling systematic errors in experiments

We acknowledge that errors occurred in a quantitative analysis are of crucial importance. It is said that *no quantitative results are of any value unless they are accompanied by some estimate of the errors inherent in them.* In fact, there are three kinds of errors in our quantitative analysis, namely **gross**, **systematic** and **random**.

Examples of gross errors are:

- a complete instrument malfunctioning without prior knowledge
- using a wrongly labelled standard reagent for analysis, such as using a labelled 0.1M NaOH with actual concentration of 0.05M
- serious deviation of standard method procedures leading to unacceptable test results

Gross errors are so serious that there is no alternative but to abandon the experiment and making a completely fresh start.

Repeated analysis results provide an idea of how precise is the analysis, i.e. the spread of test results over the average (mean) value. We say random errors lead to *replicate results differing from one another, so that the individual results fall on both sides of the average value*. Hence, random errors affect the **precision**, or **repeatability** of the experiment or the test method and are estimated by its standard deviation or variance.

But, in most analytical experiments, we ask a more important question, that is how far is the result from the true value of the concentration or amount that we are trying to measure? This is expressed as the **accuracy** of the experiment or the test method.

The ISO definition on accuracy is: *the closeness of agreement between a test result and the accepted reference value* of the analyte or measurand. Hence, under this definition, the accuracy of a single result may be affected by both random and systematic errors. Even in the absence of systematic error, the average result will probably not exactly be equal to the reference value, because of the occurrence of inherent random errors.

A significant deviation of the average result from its reference value is called bias, i.e. $b = \bar{x} - \mu$, which can be easily overlooked if we are not careful enough. Let's first discuss how systematic errors arise, and how they may be encountered.

It is important to accept the following facts :

- systematic errors cannot be revealed merely by making repeated measurements;
- unless the true result of the analysis is known beforehand (an unlikely situation), very large systematic errors might occur but go entirely undetected unless suitable precautions have been taken in the analysis.

Some sources of systematic error are:

- false assumptions made about the accuracy of an analytical instrument or a measuring apparatus.

    - For example, very simple devices such as volumetric glassware, stopwatches, pH meters and thermometers can all show substantial systematic errors but we tend to use them as though they are without bias. Also modern analytical instrument systems are now wholly controlled by computers, minimizing the number of steps and the skill levels required but we tend to regard results from these instruments as beyond reproach. In fact, they are still subject to systematic errors.

- due to human bias.

    - Some analysts suffer from astigmatism or color-blindness which might introduce errors into their readings of instruments or other observations such as end point determinations in titrations.

- possible cross contamination of targeted analyte from the use of certain apparatus such as syringes, tube caps, laboratory ware and so on, due to leaching. In here, we treat them as methodological systematic errors.

Several approaches to this problem are available, and any or all of them should be considered in each analytical procedure.

1. Consider carefully each stage of experiment to be performed, the apparatus and/or analytical instruments to be used and the sampling and analytical procedures to be adopted. We need to look for potential sources of systematic error, such as instrument calibrations, and certain steps of the analytical procedure where errors are most likely to occur.

2. Carefully plan the experiment during a new test method development and look for several possible variations of the procedures to test the robustness and ruggedness of the method in order to eliminate systematic errors.

3. The most formidable protection against systematic errors is using certified standard reference materials and standard methods for comparison through statistical tests. Before the start of each experiment, make sure that each piece of apparatus is calibrated by an appropriate procedure, such as checking the spectrometer wavelength scales and accuracy of absorbance scales, volumetric equipment, etc.

A further check on the occurrence of bias in a method is to compare the results with those obtained from a totally different method. If two unrelated methods are used to perform one analysis, and if they consistently yield results showing only random references, it is a reasonable presumption that no significant systematic errors are present. For this approach to be valid, we have to make sure that each step of the two analyses has to be independent and totally different chemistry in measurements. For example, we may compare the results obtained by an atomic-absorption spectrometric and by a colorimetric techniques.

Sometimes we may not realize about our own systematic error until we participate in an inter-laboratory cross-check or a proficiency testing program and find out that our reported results are outliers when comparing with the results given by other laboratories statistically.

When a systematic error is found in the test method or experiment, we have to investigate the cause(s) and try to eliminate them as far as possible. If for whatever reasons that such elimination is not possible, we must then estimate how much the bias from a known or true value is and make a correction factor to have the final result reported. For example, if the final mean result is 95% of the true or assigned value after a significance test, then the correction factor is 100/95 or 1.052.