Sources of Chemical Measurement Uncertainty

As a chemical analysis seldom involves only one or two steps, there are undoubtedly many uncertainties along the way. Each of them has to be carefully evaluated and a decision has to be made on whether each and every one of them is significantly large enough to affect the final results.

In general, sources of uncertainty usually involved in analytical chemistry are but not limited to :

a. Effects of sampling procedure in obtaining a representative sub-sample from a given sample for analysis, particularly when the sample is not homogeneous;
b. Sample preparation steps involving:
    - incomplete extraction of analyte or dissolution of analyte in solution
    - decomposition or degradation of the analyte during preparation through exposure to air or light
    - volatility of the analyte which may have escaped from the sample during concentration prior to the final analysis
    - efficiency of a derivatization process (chemical effects)
    - analyte absorbed on the walls of the reaction vessels and tubing, such as fluoride ion on glass vessel
    - possible diluting errors, particularly involving high dilutions
    - concentration effect to achieve low detection limits
    - control of speciation effects (e.g. total Hg, inorganic Hg, methyl mercury)
    - sample cross contamination
c. Environmental and storage conditions (such as holding time, temperature, pressure, etc) for the samples prior to analysis
d. Incomplete definition of the analyte to be analyzed - e.g. Cr(III) and Cr(IV)
e. Matrix effects and interference by other elements of the matrix
f. Reagent purity
g. Personal bias – e.g. colour blindness, possibility of reading a scale consistently high or low, any other systematic errors
h. Uncertainty in purity of certified reference material (CRM)
i. Any mismatch of CRM to sample under analysis
j. The calibration process introduces some uncertainty, including instrumental calibration uncertainty using a CRM and the instrument precision
k. The actual analysis for measurement result itself:
    - repeatability of the measurement
    - drift of the instrument parameters
    - basic instrumental background interference
    - sample carry-over in auto-analyzer due to instrumental column effects and resolutions, such as in GC and HPLC runs
    - interference caused by incomplete selectivity
    - incomplete knowledge of the influence of the environmental conditions
l. Approximations and assumptions incorporated in the test methods
m. Variable performance of the chemists and technicians

Any of these uncertainty sources once identified have to be quantified as much as possible. In chemical analysis, some of them can be difficult or even impossible to be quantified due their complex nature. In such cases, we may have to take note during the estimation of the measurement uncertainty and nothing much can be done about it.