

# **The Estimation of Uncertainty by the Utilization of Validation and Quality Control Data**

**Greg O'Donnell and Robert Geyer**

**WorkCover NSW  
Laboratory Services Unit,  
5a Pioneer Ave  
THORNLEIGH  
NSW 2120  
AUSTRALIA**

**Ph: (02) 9484-6655 Fax (02) 9980-6849**

**Email : [greg.odonnell@workcover.nsw.gov.au](mailto:greg.odonnell@workcover.nsw.gov.au)  
: [robert.geyer@workcover.nsw.gov.au](mailto:robert.geyer@workcover.nsw.gov.au)**

## **Introduction**

This protocol was developed to estimate the uncertainty of measurement of a chemical analysis by utilizing in-house validation studies and quality control data. The approach is outlined in the ISO "Guide to the Uncertainty of Measurement" (GUM)<sup>1</sup> and the EURACHEM/CITAC "Guide Quantifying Uncertainty in Analytical Measurement 2<sup>nd</sup> Ed"<sup>2</sup> and various other publications on the subject<sup>3,4,5,6</sup>. The approach was to generate an estimate of the uncertainty across the analytical concentration range. This was to be expressed as a mathematical equation or factor that could be inserted into a Laboratory Information Management System (LIMS) and thus produce an uncertainty estimate from an entered analytical result.

## **Procedure**

This approach was developed to be applicable to "calibration chemistry" and not "stoichiometric chemistry" as "calibration chemistry" is greater than 95% of the analysis performed in our laboratory. Calibration chemistry is based on having a standard and making a calibration curve with it, then isolating the analyte, and quantifying the analyte against that curve<sup>7</sup>.

The approach therefore looks at the two streams of the analysis

1. The calibration process
  2. The sample analysis process
- as illustrated below in Figure 1 :-

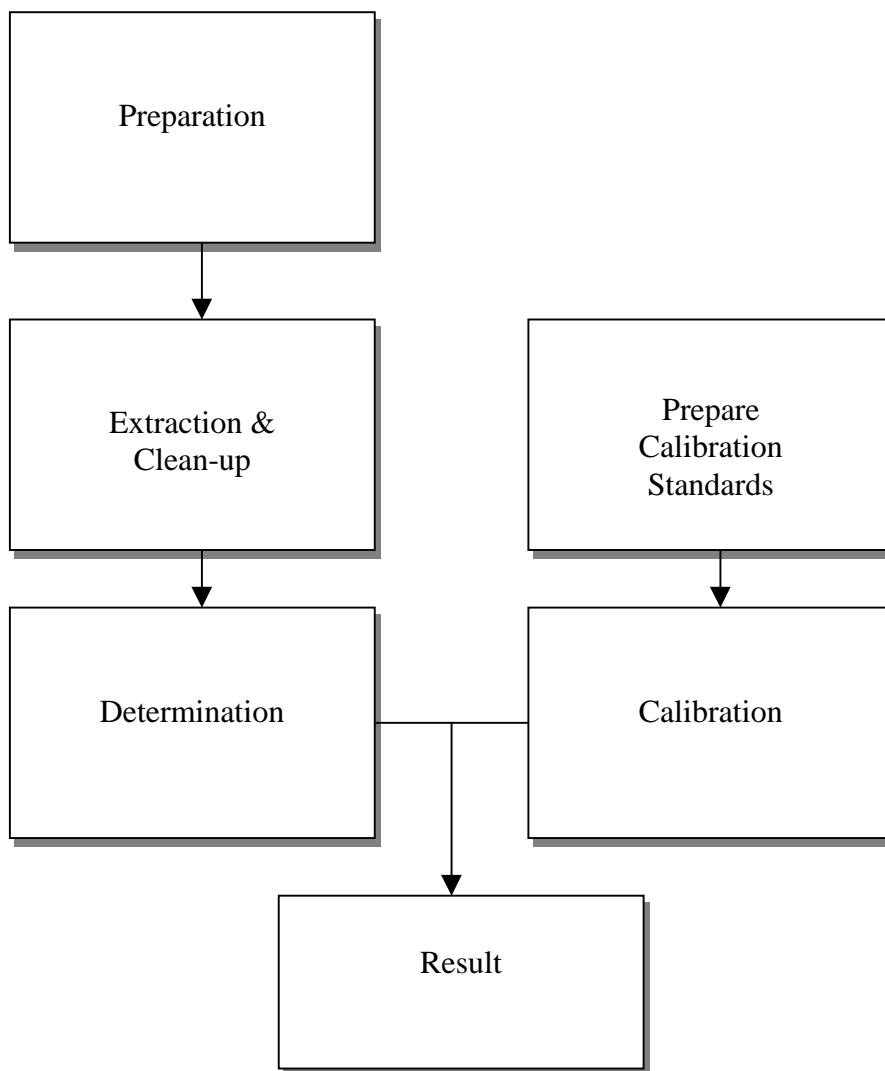


Figure 1. General analysis procedure of calibration chemistry.

The aim is to identify as many sources of uncertainty as possible and account for them by appropriate precision and trueness studies. Any additional sources of uncertainty can be evaluated by other means such as calibration certificates, published data, etc.. It may not be necessary to evaluate every source of uncertainty if they are deemed insignificant, unless there are a large number of them. Uncertainty components that are less than one third of the largest component need not be evaluated in detail. A preliminary estimate of the contribution of each component or combination of components to the uncertainty should be made and those that are not significant eliminated. The uncertainty contributions need to be expressed as standard deviations, and combined according to the appropriate rules, to give a combined standard uncertainty. The appropriate coverage factor (usually 2) should be applied to give an expanded uncertainty<sup>2</sup>. The uncertainties can be shown for convenience on an Ishikawa (cause and effect) diagram as illustrated in Figure 2.

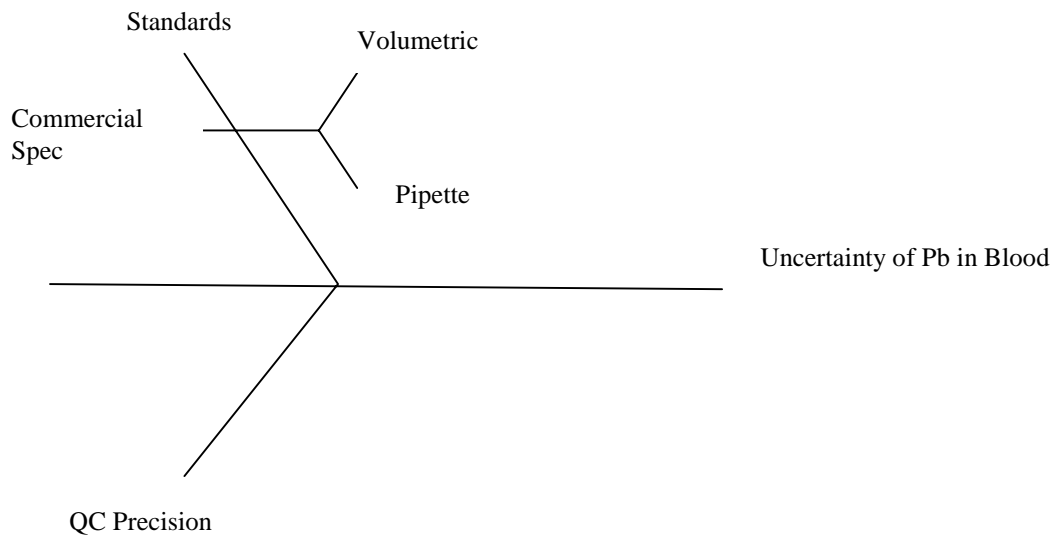


Figure 2. An Ishikawa (cause and effect) diagram of the uncertainty budget

The calculation of uncertainty process is illustrated in the examples attached

1. The analysis of lead in blood by graphite furnace atomic absorption spectrophotometry (GFAAS).
2. The analysis of glutaraldehyde in air
3. The analysis of 2,4-D herbicide in urine

## **References**

1. ISO (1993) Guide to the expression of uncertainty in measurement. ISO. Geneva, Switzerland
2. EURACHEM/CITAC (1995) Guide Quantifying uncertainty in analytical measurement 2<sup>nd</sup> Edition 2000
3. Barwick V. J., Ellison S.L.R. VAM Project 3.2.1 Development and Harmonisation of Measurement Uncertainty Principles. Part (d): Protocol for uncertainty evaluation from validation data.
4. Barwick V. J., Ellison S.L.R. Accred Qual Assur (2000) 5: 47-53
5. Barwick V. J., Ellison S.L.R. Accred Qual Assur (2000) 5: 104-113
6. Rosslein M. Accred Qual Assur (2000) 5: 88-94
7. Horwitz W. Journal of AOAC International (1998) Vol.81, No.4, 785-794