Detection Limit Procedure Based on Hubaux-Vos from USEPA Office of Groundwater and Drinking Water

September 2005

To determine the presence or absence of a contaminant a detection limit may be estimated using a procedure similar to that proposed by Hubaux and Vos [1]. A benefit of this multi-level fortification procedure is that one can estimate a detection limit in various matrices from the same data used to estimate a quantitation level known as the lowest concentration minimum reporting level (LCMRL) determination [2].

Hubaux-vos Detection Limits.

The Hubaux-Vos detection limit procedure uses a graphical solution to determine two sensitivity limits, a signal level, *y*c, and a detection limit, L_D (see Figure.) The first limit, *y*c, concerns signals that will lead to a decision whether the analyte is present or not with a certain level of confidence. Hubaux and Vos say that *y*c corresponds to L_C as defined by Currie as the critical concentration that a measured value can be said to be statistically different from zero with a probability of less than or equal to value of α. The second limit, L_D, specifies the concentration which will be detected without confusion with blanks, that is, a concentration at which an analyte that is truly in a sample will be detected about L_C with a probability of error of less than β.

It is suggested that at least 7 replicate samples at a minimum of 4 concentration levels in the matrix of interest be processed through entire method procedure. At a minimum there should be 4 replicates at any level with a total of at least 20 samples. The data is plotted as measured versus true concentration in the Figure. Constant variance is tested as described in Attachment A. If variance is found to be constant, ordinary least squares is used to generate a regression line. If variance is found to be non-constant, then variance weighted least squares is used for the regression. A regression line is drawn and two prediction limits are included with a chosen level of confidence of α for the upper prediction limit and β for the lower prediction limit. The prediction intervals have a total confidence level of 99%, such that $\alpha = 0.005$ and $\beta = 0.005$.

The point where the upper prediction interval line crosses the y-axis is the decision limit, *y*c, which is the point of lowest measurable signal that has a risk of α % that the analye is present when it is absent. A line is drawn parallel to the x-axis from *y*c to the line of the lower prediction interval and a perpendicular is dropped to the x-axis that yields a concentration of L_D. L_D is the detection limit. For a given method and a given number of fortified samples the L_C and L_D can vary as α and β are chosen according to acceptable levels of risk.

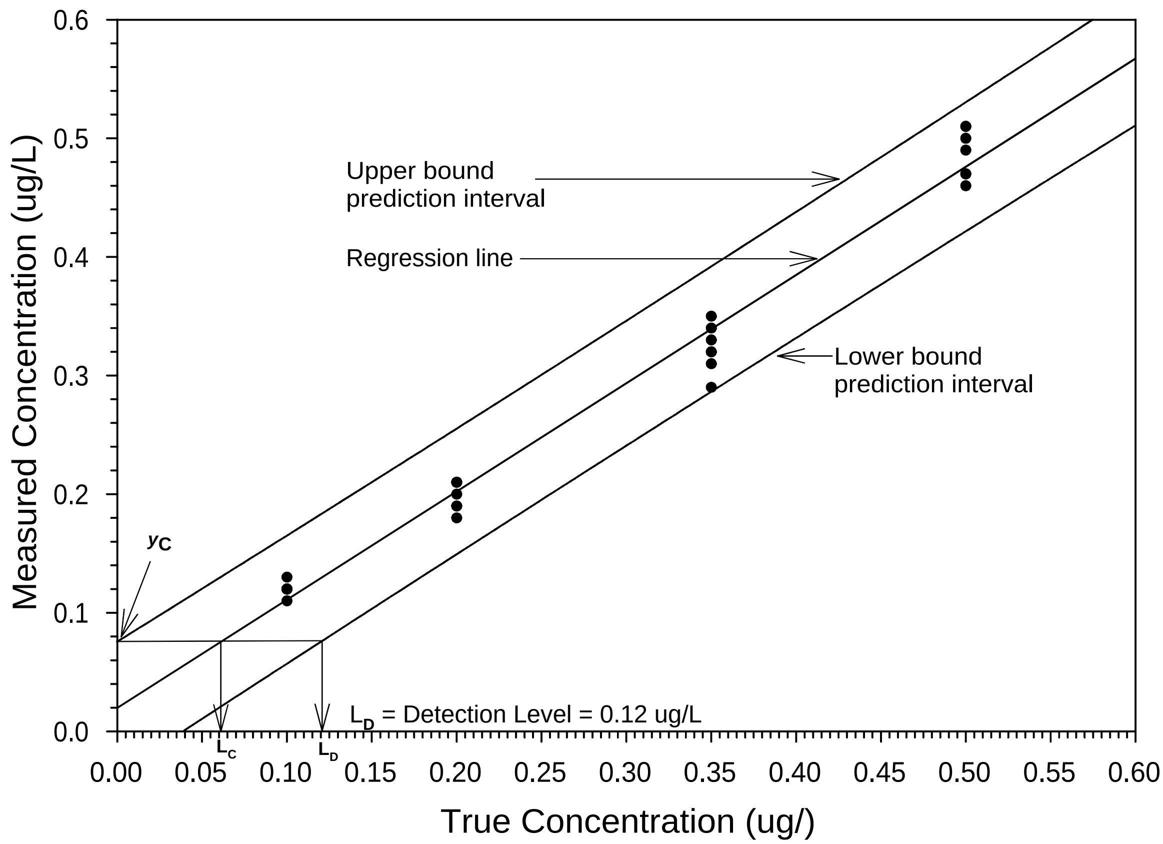

Figure: A determination of detection limit using a Hubaux-Vos graph.

Variance Weighted Least Squares for Hubaux-Vos Plot.

Variance weighted least squares (VWLS) must be used for the regression if the variance is found to be non-constant over the evaluated range. For VWLS the response variance must be modeled because the prediction intervals must be extended to the y-axis. OGWDW uses the straight-line model for the standard deviation. The Hubaux-Vos VWLS procedure first calculates the standard deviation at each true level and determines a straight-line regression from these values. The weights to be used are the inverse of the square of the standard deviation using the equation at that true value, divided by the square of the mean of the standard deviations.

Hubaux-Vos and LCMRL Graph.

The data collected for the LCMRL can also be used for the Hubaux-Vos plot. The same graph of measured versus true concentration could be used for both procedures.

When the results of fortified samples are found to be very accurate, the DL could be quite close to the LCMRL. In such a case, since there is measurement uncertainty in the region being evaluated, it might be possible that the DL be slightly higher than the graphical LCMRL. In such a case, the DL should be the lower limit of the LCMRL.

References

1. Hubaux, A., Vos, G., Decision and detection limits for linear calibration curves. *Anal. Chem.*, **42**, 8 (1970) 849-855.

2. LCMRL protocol, at website http://www.epa.gov/safewater/methods/sourcalt.html

3. Weisberg, S. *Applied Linear Regression*; John Wiley & Sons: Second Edition, 1985.