Detect

Detect is the most advanced computer program for the computation of detection and quantification limit estimates. Detect can compute both detection and quantification limits from either single concentration data or calibration based data (ie multiple concentrations). In all cases, calibration based approaches are preferable in that they remove the confound between the estimated detection or quantification limit and the concentration at which the samples were spiked. A major strength of the Detect program is that it can simultaneously model the relationship between true concentration and measured concentration and the relationship between true concentration and measurement variability using weighted least squares (WLS). Detect computes both the critical level (LC) and the detection limit (LD) for each calibration based estimator. Detect can compute detection limits based on either prediction limits or tolerance limits. Detection limits based on prediction limits provide 99% confidence for the next single detection decision whereas detection limits based on tolerance limits provide 95% confidence of including 99% of all future detection decisions.

Detect can automatically compute the following detection limit estimators:

Single Concentration Estimators

- USEPA MDL
- Currie's LD

Calibration Based Estimators

- Hubaux and VOS LC and LD
- Approximate WLS LC and LD based on prediction limits
- Iterative WLS LC and LD based on prediction limits
- Approximate WLS LC and LD based on tolerance limits
- Iterative WLS LC and LD based on tolerance limits

In terms of quantification limits, Detect can compute:

Single Concentration Estimators

- USEPA "Minimum Level" (ML)

Calibration Based Estimators

- The "Alternative Minimum Level" (AML)
- Iterative version of Currie's "Determination Limit" (LQ)

Detect automatically provides graphical output of (1) the recovery curve, (2) the association between true concentration and variability (modeled either as an exponential regression or using the Rocke and Lorenzato model), (3) the relationship between true concentration and the percent relative standard deviation and (4) tabular output giving the 99% prediction bounds at evenly spaced concentrations in the calibration range. For each model, a complete computational worksheet is also provided.

OVERVIEW

The detection limit is a statistical estimate that is used to make the binary decision of whether or not the true concentration in a given sample is greater than zero. A frequent confusion regarding the detection limit is that measured concentrations exceeding the detection limit are quantifiable (i.e., the estimated concentration can be reliably determined). This is not the case. Measured concentrations above the detection limit only allow one to conclude that the analyte is present in the sample at a concentration greater than zero. Quantification limits (also known as quantitation limits) have been developed for the purpose of quantitative determination (Currie 1968 and Gibbons et. al., 1992) and are also provided in Detect. Currie (1968) defined the "detection limit" LD as the true concentration "at which a given analytical procedure may be relied upon to lead to a detection." Note that the emphasis here is on "true concentration" and not measured concentration. Currie also defined the "critical level" LC as the measured concentration "at which one may decide whether or not the result of an analysis indicates detection".

It is important to understand the difference between LC and LD. When the true concentration is equal to LC the probability of detecting it is only 50%. In contrast, when the true concentration is at the LD the probability of a measured concentration below LC (hence a non-detection) is 1%. The detection limit LD may be relied upon to lead to a detection in 99% of the cases, whereas the critical level leads to a detection only half of the time. As an analogy, the critical level for the federal speed limit is 55 mph, however, police will rarely identify an exceedance until a driver exceeds 60 mph and their confidence that the true speed (not just the measured speed) has exceeded the limit is high. There are many different names for detection and quantification limits which can lead to confusion. Often, the detection limit is confused with the critical level. Furthermore, there are diverse views about the choice of statistical multiplier, use of blanks, and single concentration versus multiple concentration calibration design. Unfortunately, different investigators have also given different names to the various statistical approaches to estimating the same thing. While the distinction between the critical level and the detection limit are qualitative and are therefore deserving of different names, the other distinctions are not.

Detect provides several statistical approaches to estimating both the detection limit LD and the quantification limit LQ. The choice among these different estimators should be based on the different assumptions made by these methods, the suitability of which can be determined from empirical data. Single concentration based estimators such as USEPA's Method Detection Limit (MDL) and Minimum Level (ML) and Currie's LD are also provided in Detect for completeness; however, they generally should not be used in practice because the results are highly dependent on the concentration at which the samples are spiked. Similarly, the Hubaux and Vos (1970) procedure is also included in Detect because of its historical importance as the first calibration based detection limit estimator. Note, however, that the Hubaux-Vos method assumes constant variability over the entire calibration range and will therefore routinely lead to overestimates of the true detection limit since it must overestimate variability at low levels in order to accommodate variability at higher levels. The remaining detection limit estimators in Detect can be categorized in terms of approximate versus iterative solution based on prediction limits versus tolerance limits. These four models all assume that variability is a function of concentration and as such direct solution for LD which is a function of variability at LD is not possible.

Two solutions are possible. First, Gibbons et. al., (1991) (also see Gibbons 1994 and 1995 and Oppenheimer et. al., 1983) describe an approximate solution in which variability at the lowest spiking concentration is used in anchoring the detection limit. Second, using a model for the relationship between concentration and variability (e.g., an exponential model or the Rocke and Lorenzato model, 1995) we can iteratively solve for LD. This more exact solution should be used in practice. The second choice involves use of a prediction limit (PL) versus a tolerance limit (TL). Detection limits based on prediction limits apply to the next detection decision only. By contrast, detection limits based on tolerance limits apply to the entire population of detection decisions and provide a specific level of confidence of including a specified proportion of all future detection decisions. In Detect, detection limits based on tolerance limits will cover 99% of all future detection decisions with 95% confidence. For this reason, detection limits based on tolerance limits are recommended for routine applications in which a large and potentially unknown number of future detection decisions are made on the basis of a single detection limit study.

In terms of quantitative determination, Detect provides three different estimators; the USEPA Minimum Level (ML), the Alternative Minimum Level (AML, Gibbons, Coleman and Maddalone, 1996) and an iterative version of Currie's (1968) Determination Limit (LQ). The ML is a single concentration based method and is provided in Detect for illustrative purposes only. The iterative LQ estimator is the most statistically appealing in that it solves for the true concentration at which the signal to noise ratio is 10:1 (i.e., a percent relative standard deviation (%RSD) of 10%). However, if the rate of change in SD as a function of concentration is greater than .1, the LQ is not defined and the iterative solution will not converge. Detect deals with this problem by testing for convergence and if the model does not converge, 2.5% is added to the required %RSD (i.e., 12.5% RSD) and the process is repeated until a %RSD is identified that leads to convergence. In this way, the lowest possible %RSD is identified and the corresponding concentration estimated. Finally, the AML provides a good compromise between the ML and iterative LQ by initially anchoring the estimate of the standard deviation at the estimate of LC (i.e., the critical level) which is the lowest concentration that is differentiable from zero. The AML is then estimated as the upper prediction limit for the true concentration that is 10 times the standard deviation at the critical level. Note that in estimating the prediction limit, we use the estimated standard deviation at the provisional estimate of the AML (i.e., 10SLC). As such, although the AML does not guarantee a %RSD of 10% it will typically provide a %RSD of approximately 10% and the actual %RSD at the AML is automatically computed by the program. The AML is the quantification limit estimator that is recommended for routine application.

TECHNICAL CONSIDERATIONS

The detection limit is a statistical estimate that is used to make the binary decision of whether or not the true concentration in a given sample is greater than zero. A frequent

confusion regarding the detection limit is that measured concentrations exceeding the detection limit are quantifiable (i.e., the estimated concentration can be reliably determined). This is not the case. Measured concentrations above the detection limit only allow one to conclude that the analyte is present in the sample at a concentration greater than zero. Quantification limits (also known as quantitation limits) have been developed for the purpose of quantitative determination (Currie 1968 and Gibbons et. al., 1992) and are also provided in Detect. Currie (1968) defined the "detection limit" LD as the true concentration "at which a given analytical procedure may be relied upon to lead to a detection." Note that the emphasis here is on "true concentration" and not measured concentration. Currie also defined the "critical level" LC as the measured concentration "at which one may decide whether or not the result of an analysis indicates detection".
It is important to understand the difference between LC and LD. When the true concentration is equal to LC the probability of detecting it is only 50%. In contrast, when the true concentration is at the LD the probability of a measured concentration below LC (hence a non-detection) is 1%. The detection limit LD may be relied upon to lead to a detection in 99% of the cases, whereas the critical level leads to a detection only half of the time. As an analogy, the critical level for the federal speed limit is 55 mph, however, police will rarely identify an exceedance until a driver exceeds 60 mph and their confidence that the true speed (not just the measured speed) has exceeded the limit is high. There are many different names for detection and quantification limits which can lead to confusion. Often, the detection limit is confused with the critical level. Furthermore, there are diverse views about the choice of statistical multiplier, use of blanks, and single concentration versus multiple concentration calibration design. Unfortunately, different investigators have also given different names to the various statistical approaches to estimating the same thing. While the distinction between the critical level and the detection limit are qualitative and are therefore deserving of different names, the other distinctions are not.