° Detection Limits and Related Topics

° Whether or not a quantity is above background levels is a critical issue in environmental restoration.

° Environmental organizations attempt cleaning contaminated sites until only normal background levels of pollution remain.

° How and when can we say that chemical specie in a measured sample is above background.

° This issue is called a detection limit issue.

° In many areas of science particularly environmental chemistry the reporting of some type of detection limit is routine.

° Examples:

Definition1. <u>Lower Limit of Detection (LLD)</u>. "The LLD is defined, as the smallest concentration of the radioactive material in a sample that will yield a value above background, that will be detected with 95% probability with only 5% probability of concluding that a blank observation represents a "real" signal." (1)

Definition 2. Instrumental Detection Limit (LDL). "The concentration equivalent to a signal, due to an analyte, which is equal to three times the standard deviation of a series of ten replicates of a reagent blank signal measured at the same wavelength." (2)

See (3) for many more regulatory definitions and references.

° Labs should always report their trimming (detection) rule regardless of which one they choose. This will eliminate confusion caused by the many regulatory definitions of detection limits

° Secondly it is clear that using detection limits destroys information (below the detection limit) that may be useful in some later studies. Therefor labs should make the original data available to future investigators. Otherwise valuable information will be wasted.

° Let us denote our measurement(s) by Y.

The data may be a scalar, vector (a single chemical spectra), or a matrix (a collection of spectra.)

° We are going to estimate something:

Here we use a couple of choices:

We may wish to estimate the true concentration of a chemical species or the mean of a large number of replicate measurements.

On the other hand we may wish to predict another measurement.

° Whatever we try to estimate we call it Θ.

Our estimate will depend upon the data (and our other knowledge). We denote our estimator as d(Y).

Following statistical tradition we specify a loss function. There is a loss for every incorrect decision and usually the more a measurement is in error the large the loss. Our loss function is denoted by L(d(Y),Θ).

There are two more ingredients in our framework. We need the probability distribution of our measurements given Θ. We denote it by $F(Y|\Theta)$.

Often this is just the distribution of our random error, but sometimes it includes bias.

The final (but important) ingredient is a probability distribution for Θ. We denote its density by $p(\Theta)$. It specifies the ranges and likelihood for Θ. It is called a prior distribution as it summarizes what we know about Θ before we collect the data. In what follows precise knowledge about $p(\Theta)$ is not necessary.

° Finally we say that an estimator $\hat{d}(Y)$ is <u>inadmissible</u> (with respect to the definitions above) if there exists an estimator $d^*(Y)$ such that $\int L(d^*(Y),\Theta)\, dF(Y|\Theta) \leq \int L(\hat{d}(Y),\Theta)\, dF(Y|\Theta)$ for all Θ and the inequality is strict for at least one value of Θ.

° An estimator that is not inadmissible is admissible. Inadmissible estimators have some other estimator rule that is at least as good for all values of Θ and better for at least one value of Θ.

° However, there are estimators that are inadmissible with respect to a particular loss function that are still reasonable. This will be demonstrated as we proceed.

Experiments that can be performed at your desk:

° Example 1.Consider a pencil on a table. If you push one end it should move according to Newton' law F = m a. Assume that you know the weight, acceleration due to gravity, and duration of the time, and speed of the pencil. Then you may calculate the total amount of force applied to the pencil. However, if you apply a slight force to the pencil it may not move. We find that slight forces produce no response. The problem is not Newton's laws but rather that static coefficient of friction is not accounted for in our calculation.

° Example 2. Nuclear weapons produce light and the larger the amount of fissionable material the more light they produce. Since the age of atmospheric nuclear weapons testing it is believed that all human beings possess some fissionable material in their bodies. Yet we produce no light as the amount of fissionable material is well below the critical mass needed for such a reaction.

Fortunately, for your body the amount is too small to estimate this way.

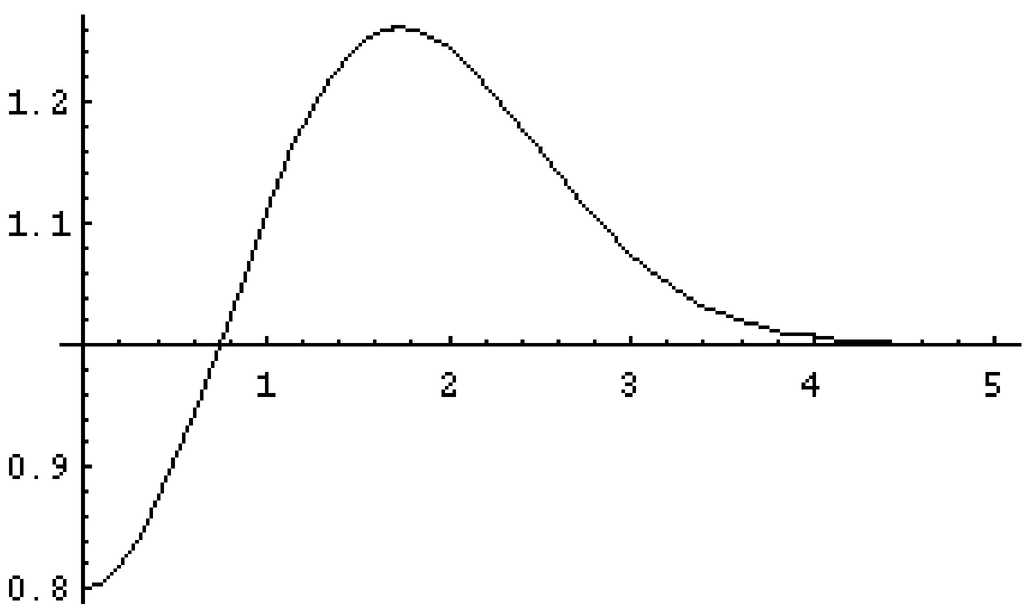
° We start with squared error loss, the most common loss function used in estimation.

Suppose we use squared error loss

$$L_2(c,\hat{c}) = |\hat{c} - c|^2.$$

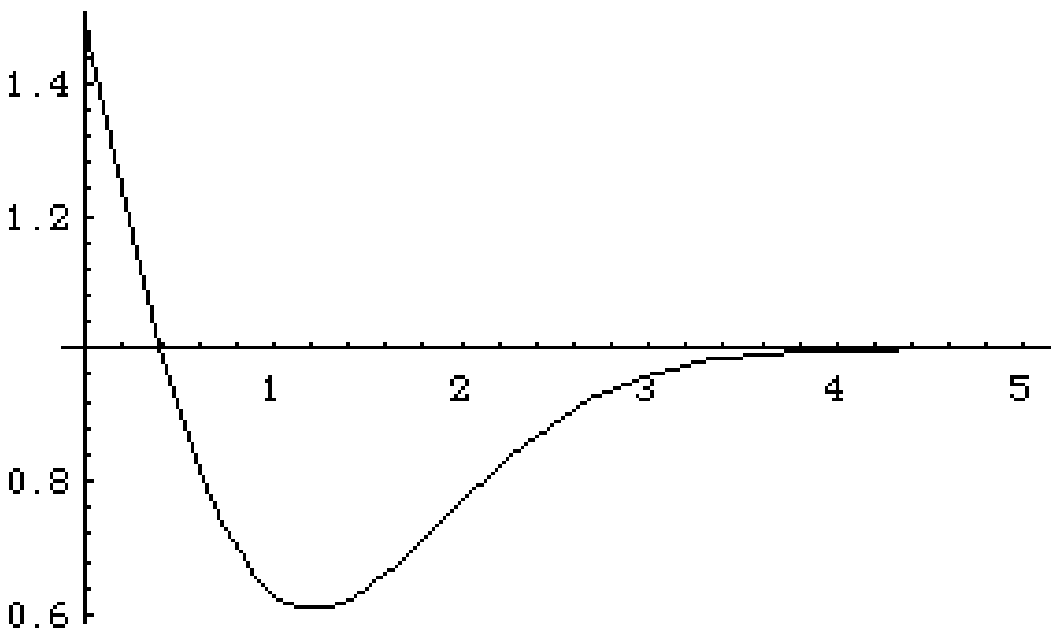
Lets look at the following rule

Report $\hat{c}$ if it is bigger than 1 otherwise report 0.



Of course there are other ways to report detectio rules.

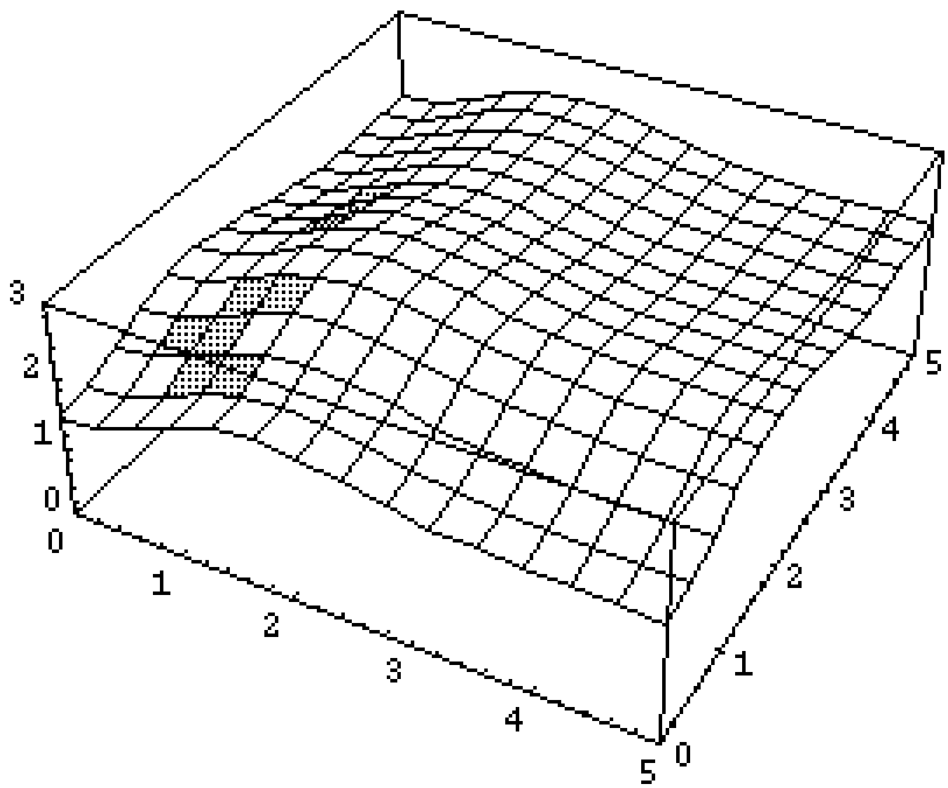
Report $\hat{c}$ if it is bigger than 1 otherwise report 1.



Now suppose that we wish to follow a trend.

We take two measurements and our loss is squared error loss for the difference of c_1 and c_2.

Then we get losses that look like



The point is that if we deal with very small quantities we are well off using rounding.

If the concentrations are very high we do OK.

If the values are in the middle then we are better off by not rounding.