Calibration Curves

Calibration relates instrument response to standard values

Data is collected in two stages:

1. Training stage (calibration experiment)

2. Measurement stage (instrument response)

Step 1. Collecting the calibration data and modelling the calibration curve

The data is (x_i, Y_i), $i = 1, \ldots n$.

In the usual statistics tradition x_i denotes the chosen standards (Predictors) and Y_i denotes the instrument response. Chemists sometimes interchange the notation. In addition c (concentration) is often substituted for x.

In the beginning we assume a straight line homoscedastic model.

$Y_i = \alpha + \beta x_i + \sigma e_i$

and our goal from the first stage is to

1. Choose the x_i

2. Estimate α, β , and σ.

Second stage

We collect instrument responses Z_i of unknown x_i values.

Provide point and interval estimates of the x_i values.

There are many possibilities.

Absolute calibration:

A quick or nonstandard method is calibrated against a standard or defined measurement.

Comparative calibration:

One instrument or measurement technique is calibrated against another. Neither is inherently standard. Last chapter.

How is the Calibration Curve Used?

Single use: Here separation of 2 calibration steps is artificial.

Multiple use: Lots of dependent measurements.

Used in combination with other measurements?

Who produces the calibration curve or does the calibrator do both steps 1 and 2?

Designed or natural calibration experiment?

Designed calibration experiments are typical of laboratory chemistry

Natural calibration occurs in observational chemistry areas such as environmental chemistry.

Are the Z_i arbitrary or natural?

Arbitrary implies no prior knowledge about where the Z's come from and is typical of a frequentist set up.

Natural implies some prior distribution about the Z's.

Absolute calibration:

In what direction should the curve be fit?

Most calibration literature deals with this issue. For precision instruments the fitting direction makes very little difference.

What is the point estimate? Interval estimate for a single use?

The MLE is the standard estimate: $\hat{\xi} = \dfrac{Z - \hat{\alpha}}{\hat{\beta}}$.

Properties: It has no mean and no variance but using propagation of error formulas approximate formulas are found.

There is some confusion in the literature as to what the correct expressions for mean and variance are.

From Naszódi(1978) $\tilde{\mu}_{\hat{\xi}} = \xi + \dfrac{\sigma^2(\xi-\bar{x})}{\sum_i (x_i-\bar{x})^2}$.

The variance expressions that are found in the literature are discrepant.

Let $s^2(x) = \sqrt{\dfrac{1}{n} + \dfrac{(x-\bar{x})^2}{\sum_i (xi-\bar{x})^2}}$

The approximate answer I get is $\frac{\hat{\sigma}^2}{\hat{b}^2}(1+s^2(\xi) + \frac{\sigma^2}{\hat{b}^2\sum_i (x_i-\bar{x})^2})$

This is not the answer in Shukla(1972).

So one would guess that

$$\hat{\xi} - \frac{\sigma^2(\hat{\xi} - \bar{x})}{\sum_i (x_i-\bar{x})^2} \pm t_{(1-\alpha/2)}\sqrt{\frac{\hat{\sigma}^2}{\hat{b}^2}(1+s^2(\hat{\xi}) + \frac{\sigma^2}{\hat{b}^2\sum_i (x_i-\bar{x})^2})}$$

would be a valid 1-α confidence interval for ξ.

Applied statisticians and scientists have for many years used $\hat{\xi} \pm t_{(1-\alpha/2)}\sqrt{\frac{\hat{\sigma}^2}{\hat{b}^2}(1+s^2(\hat{\xi}))}$.

Which interval is a more valid confidence interval.

Fieller's method.

Range of parameter values effect the coverage probabilities.

Multiple use intervals.

If we have estimates

$$\hat{\xi}_i = \frac{Z_i - \hat{a}}{\hat{b}} \qquad i = 1,\ldots \text{ then these estimates are dependent.}$$

How should we get confidence intervals?

What are the components of error?

What criteria should we require from our intervals?

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