Basic calibration functions for analytical chemistry

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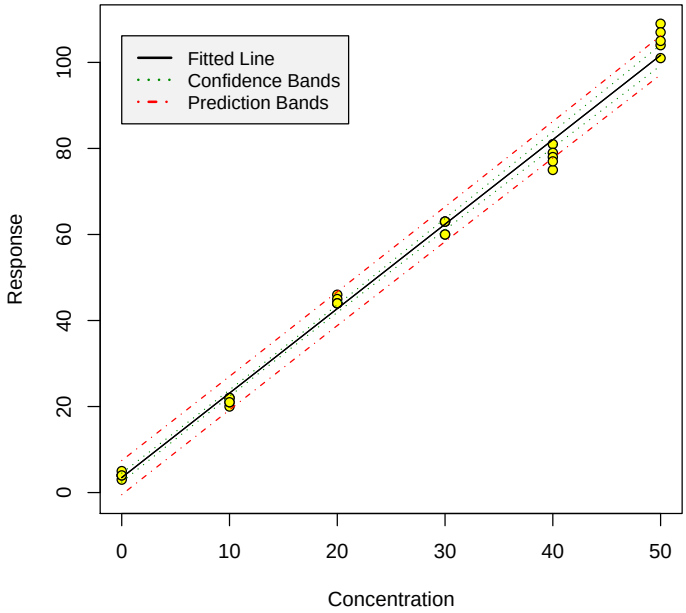
The `chemCal` package was first designed in the course of a lecture and lab course on "analytics of organic trace contaminants" at the University of Bremen from October to December 2004. In the fall 2005, an email exchange with Ron Wehrens led to the belief that it could be heavily improved if the inverse prediction method given in [1] would be implemented, since it also covers the case of weighted regression.

At the moment, the package only consists of two functions, working on univariate linear models of class `lm` or `rlm`.

When calibrating an analytical method, the first task is to generate a suitable model. If we want to use the `chemCal` functions, we will have to restrict ourselves to univariate, possibly weighted, linear regression so far.

Once such a model has been created, the calibration can be graphically shown by using the `calplot` function:

```
> library(chemCal)
> data(massart97ex3)
> attach(massart97ex3)
> yx <- split(y, factor(x))
> ybar <- sapply(yx, mean)
> s <- round(sapply(yx, sd), digits = 2)
> w <- round(1/(s^2), digits = 3)
> weights <- w[factor(x)]
> m <- lm(y ~ x, w = weights)
> calplot(m)
```



This is a reproduction of Example 8 in [1]. We can see the influence of the weighted regression on the confidence and prediction bands of the calibration.

If we now want to predict a new x value from measured y values, we use the `inverse.predict` function:

```
> inverse.predict(m, 15, ws = 1.67)

$Prediction
[1] 5.865367

$`Standard Error`
[1] 0.7288138

$Confidence
[1] 2.023511

$`Confidence Limits`
[1] 3.841856 7.888878
```

The weight `ws` assigned to the measured y value has to be given by the user in the case of weighted regression. By default, the mean of the weights used in the linear regression is used.

Theory

Equation 8.28 in [1] gives a general equation for predicting the standard error $s_{\hat{x}_s}$ for an x value predicted from measurements of y according to the linear calibration function $y = b_0 + b_1 \cdot x$:

$$s_{\hat{x_s}} = \frac{s_e}{b_1}\sqrt{\frac{1}{w_s m} + \frac{1}{\sum w_i} + \frac{(\bar{y_s} - \bar{y_w})^2 \sum w_i}{{b_1}^2\left(\sum w_i \sum w_i {x_i}^2 - \left(\sum w_i x_i\right)^2\right)}} \tag{1}$$

with

$$s_e = \sqrt{\frac{\sum w_i (y_i - \hat{y}_i)^2}{n-2}} \tag{2}$$

where w_i is the weight for calibration standard i, y_i is the mean y value (!) observed for standard i, $\hat{y}_i$ is the estimated value for standard i, n is the number calibration standards, w_s is the weight attributed to the sample s, m is the number of replicate measurements of sample s, $\bar{y_s}$ is the mean response for the sample, $\bar{y_w} = \frac{\sum w_i y_i}{\sum w_i}$ is the weighted mean of responses y_i, and x_i is the given x value for standard i.

The weight w_s for the sample should be estimated or calculated in accordance to the weights used in the linear regression.

I adjusted the above equation in order to be able to take a different precisions in standards and samples into account. In analogy to Equation 8.26 from [1] we get

$$s_{\hat{x_s}} = \frac{1}{b_1}\sqrt{\frac{{s_s}^2}{w_s m} + {s_e}^2\left(\frac{1}{\sum w_i} + \frac{(\bar{y_s} - \bar{y_w})^2 \sum w_i}{{b_1}^2\left(\sum w_i \sum w_i {x_i}^2 - \left(\sum w_i x_i\right)^2\right)}\right)} \tag{3}$$

References

[1] Massart, L.M, Vandenginste, B.G.M., Buydens, L.M.C., De Jong, S., Lewi, P.J., Smeyers-Verbeke, J. Handbook of Chemometrics and Qualimetrics: Part A, Elsevier, Amsterdam, 1997