Basic calibration functions for analytical chemistry

Johannes Ranke

June 23, 2006

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 would be desirable to implement the inverse prediction method given in [1] since it also covers the case of weighted regression. Studies of the IUPAC orange book and of DIN 32645 as well as publications by Currie and the Analytical Method Committee of the Royal Society of Chemistry and a nice paper by Castillo and Castells provided further understanding of the matter.

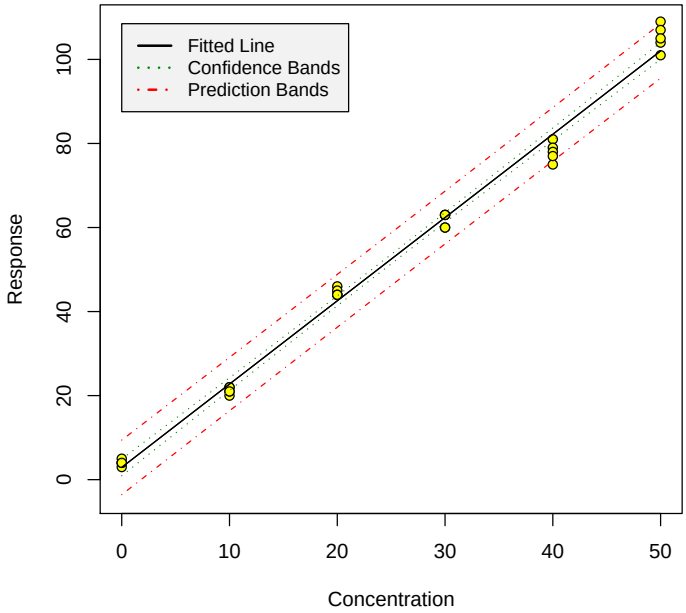
At the moment, the package consists of four functions, working on univariate linear models of class `lm` or `rlm`, plus to datasets for validation.

A bug report (PR#8877) and the following e-mail exchange on the r-devel mailing list about prediction intervals from weighted regression entailed some further studies on this subject. However, I did not encounter any proof or explanation of the formula cited below yet, so I can't really confirm that Massart's method is correct.

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.

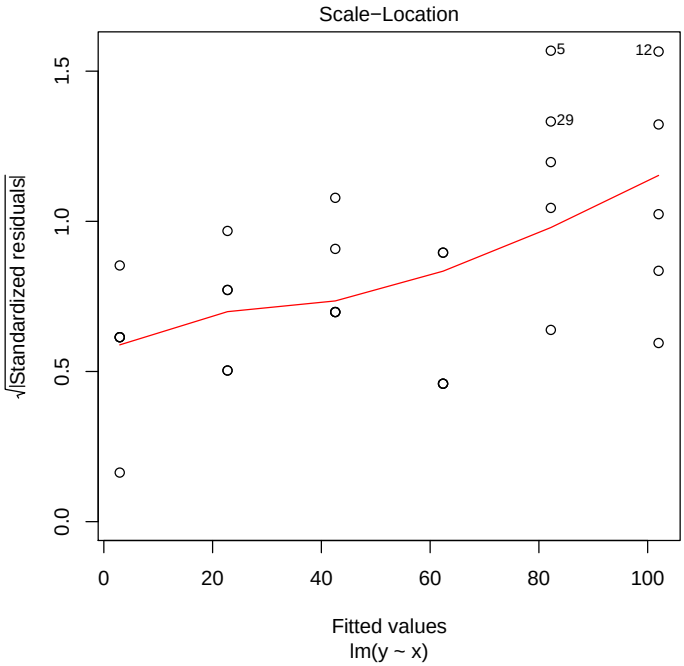
Once such a model has been created, the calibration can be graphically shown by using the `calplot` function:

```
> library(chemCal)
> data(massart97ex3)
> m0 <- lm(y ~ x, data = massart97ex3)
> calplot(m0)
```



As we can see, the scatter increases with increasing x. This is also illustrated by one of the diagnostic plots for linear models provided by R:

```
> plot(m0, which = 3)
```



Therefore, in Example 8 in [1] weighted regression is proposed which can be reproduced by

```
> attach(massart97ex3)
> yx <- split(y, 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)
```

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] 0.892611

$Confidence
[1] 2.478285

$`Confidence Limits`
[1] 3.387082 8.343652
```

```
> inverse.predict(m, 90, ws = 0.145)

$Prediction
[1] 44.06025

$`Standard Error`
[1] 2.829162

$Confidence
[1] 7.855012

$`Confidence Limits`
[1] 36.20523 51.91526
```

The weight `ws` assigned to the measured y value has to be given by the user in the case of weighted regression, or alternatively, the approximate variance `var.s` at this location.

Theory for `inverse.predict`

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

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

where I interpret $\frac{{s_s}^2}{w_s}$ as an estimator of the variance at location $\hat{x_s}$, which can be replaced by a user-specified value using the argument `var.s` of the function `inverse.predict`.

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