Basic calibration functions for analytical chemistry

Johannes Ranke

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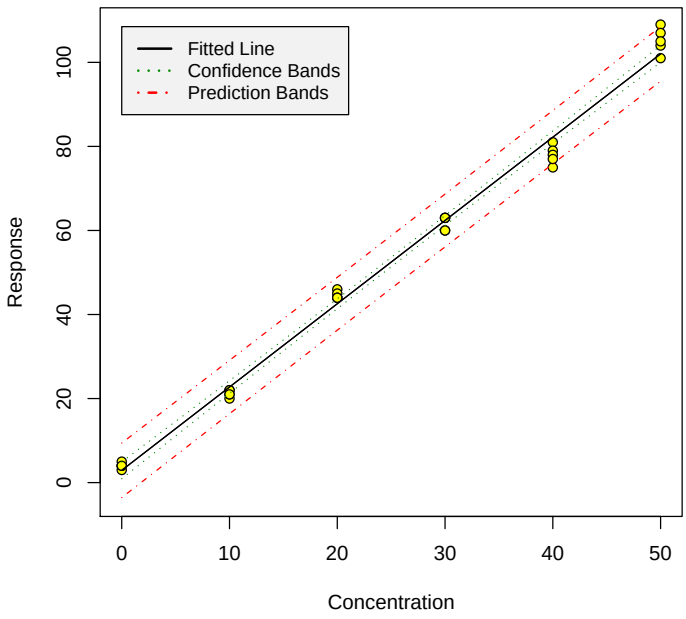
When calibrating an analytical method, the first task is to generate a suitable model. If we want to use the `chemCal` functions, we will have to restrict ourselves to univariate, possibly weighted [1], linear regression so far.

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

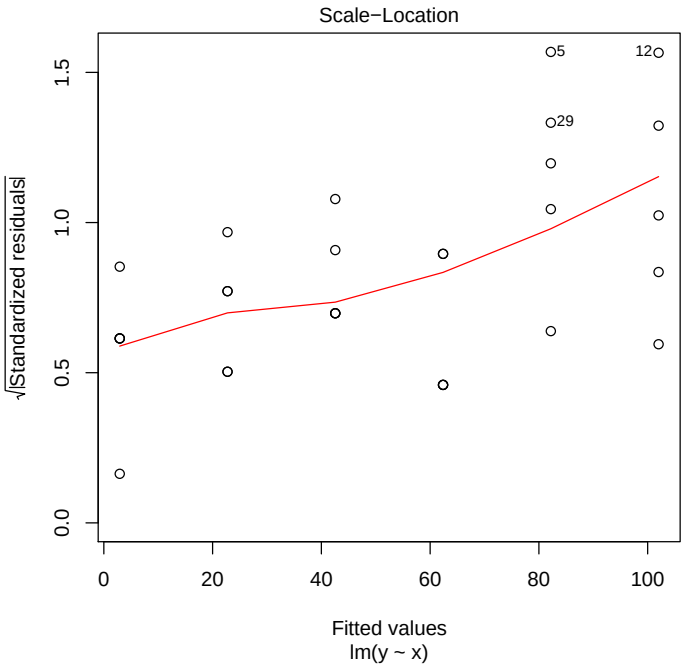
```
> library(chemCal)
> data(massart97ex3)
> attach(massart97ex3)
> m0 <- lm(y ~ x)
> calplot(m0)
```



[1] For the weighted case, the function `predict.lm` would have to be adapted (Bug report PR#8877), in order to allow for weights for the x values used to predict the y values. This affects the functions `calplot` and `lod`.

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

```
> 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)
```

Unfortunately, `calplot` does not work on weighted linear models, as noted in the footnote above.

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. By default, the mean of the weights used in the linear regression is used.

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

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

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