

PROCEDURE FOR DETERMINATION OF CALIBRATION UNCERTAINTY

Corresponding to n values of a known input x_i , we have obtained the output readings y_i of the instrument that is being calibrated.

i	x_i	y_i	\hat{y}_i	e_i	e_i^2	$(x_i - \bar{x})^2$
1	500	256	254.34	1.66	2.747	14066.0
2	431	212	216.91	-4.91	24.097	2460.2
3	370	189	183.82	5.18	26.881	130.0
4	321	155	157.23	-2.23	4.982	3648.2
5	285	138	137.70	0.30	0.089	9293.0
Sum	1907	950			58.796	29597.2
	$\sum x_i$	$\sum y_i$			$\sum e_i^2$	

We need to obtain a relationship of the form $\hat{y} = a_0 + a_1 x$. The residual error e_i at a point i may be defined as $e_i = y_i - \hat{y}_i$. To evaluate the constants a_0 and a_1 according to the least squares criterion, we need to solve the normal equations:

$$\begin{aligned} \sum y_i &= n a_0 + a_1 \sum x_i \\ \sum x_i y_i &= a_0 \sum x_i + a_1 \sum x_i^2 \\ a_0 &= -16.92 \quad a_1 = 0.5425 \end{aligned}$$

To check whether the model is good, examine the residual errors. They should be random and normally distributed without any pattern.

Now, the standard deviation of y $S_y = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\nu}} = \sqrt{\frac{\sum_{i=1}^n e_i^2}{\nu}}$; where ν is the degrees of freedom = $n-2$ for the case of a straight line fit. For the example, $S_y = 4.43$

The standard deviation for the estimate of the slope of the fit is given

$$\text{by } S_{a_1} = \frac{S_y}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2}} = \frac{4.43}{\sqrt{29597.2}} = 0.0257$$

A confidence interval for a_1 is $a_1 \pm t_{\nu, p} S_{a_1} = 0.5425 \pm 3.18 * 0.0257 = 0.4607$ to 0.6243

The standard deviation for the zero intercept is given by

$$S_{a_0} = S_y \sqrt{\frac{\sum_{i=1}^n x_i^2}{n \sum_{i=1}^n (x_i - \bar{x})^2}} = 4.43 \sqrt{\frac{756927}{5 * 29597.2}} = 10.01$$

A confidence interval for a_0 is

$$a_0 \pm t_{\nu, p} S_{a_0} = -16.92 \pm 3.18 * 10.01 = -13.9108$$
 to -47.7508

A confidence interval for the mean predicted value \hat{y} at a given value of x_j is given by

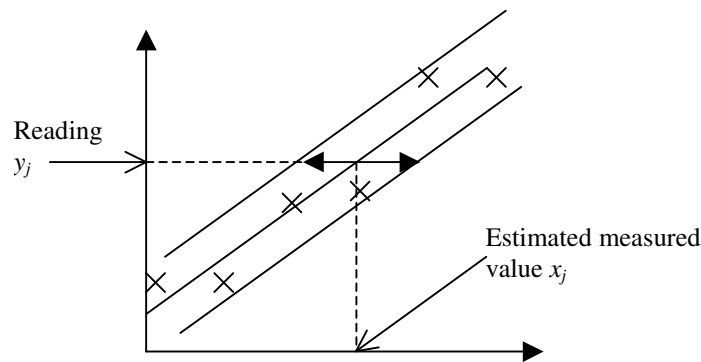
$$\hat{y} \pm t_{v,P} S_y \left[\frac{1}{n} + \frac{(x_j - \bar{x})^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right]^{1/2} \quad (P\%)$$

A prediction interval for a single value \hat{y} at a given value of x_j is given by

$$\hat{y} \pm t_{v,P} S_y \left[1 + \frac{1}{n} + \frac{(x_j - \bar{x})^2}{\sum_{i=1}^n (x_i - \bar{x})^2} \right]^{1/2} \quad (P\%)$$

During calibration, the independent variable x_i is usually a known and controlled value. Then the precision interval for a single predicted value is $\hat{y} \pm t_{v,P} S_y (P\%)$.

If this calibration equation is used to correct the observed reading, the standard deviation in the true value would be $S_x = \frac{S_y}{a_1}$. Hence the uncertainty in the measured value would be $\pm t_{v,P} S_x (P\%)$. This is the coverage interval for the calibration uncertainty with $P\%$ confidence.



The standard practice is to use 95% confidence, for which the Student's t distribution values are as follows:

ν	1	2	3	4	5	6	7	8	9	10
t_{95}	12.71	4.30	3.18	2.78	2.57	2.45	2.36	2.31	2.26	2.23
ν	11	12	13	14	15	16	17	18	19	20
t_{95}	2.20	2.18	2.16	2.14	2.13	2.12	2.11	2.10	2.09	2.09
ν	25	30	35	40	45	100	∞			
t_{95}	2.06	2.04	2.03	2.02	2.01	1.98	1.96			