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Evaluation of measurement uncertainty for thermometers with calibration equations

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Abstract The method recommended by Eurachem did not mention the effect of adequateness of calibration equations on the measurement uncertainty. In this work, the sources of measurement uncertainty for two types of thermometer were evaluated. Three calibration equations were adopted to compare its predictive performance. These sources of combined uncertainty include predicted values of calibration equation, nonlinearity and repeatability, reference source, and resolution source. The uncertainty analysis shows that the predicted uncertainly of calibration equations is the main source for two types of thermometer. No significant difference of the uncertainty was found between the classical method and the inverse method. However, the calculation procedure of the inverse method was simpler and easier than that of the classical method.

Keywords Uncertainty · Calibration equation · Nonlinearity

Introduction

The evaluation of measurement uncertainty has been adopted for researchers. Some international guidelines and recommendations have been published and extended [1, 2]. In the EURACHEM/CITAC Guide [2], four main sources of uncertainty were considered:

1. Random variations in measurement of y,
2. Random effects resulting in errors in the assigned reference values x_i,
3. Value of x_i and y_i may be subjected to a constant unknown offset,
4. The assumption of linearity may be invalid.

For the measurement works, instrument was calibrated by detecting the reading value, y, to different levels of the standard value, x. Then the relationship between y and x was established as: $y = f(x)$. The function, $f(x)$, is called the calibration equation of y. As the new measurement y_i was found, the predicted response value of X_{pred} can be computed by the calibration equation. Recently, the technique of calibration model was discussed by several researchers. Geladi et al. [3] used the multiple linear regression technique to evaluate the prediction bias of nonlinearities. The validation and prediction performance for different calibration models established by ordinary least-square, partial least squares regression, principal component analysis and ridge regression were reviewed detail by Geladi et al. [4]. The method of the transform of multivariate calibration models to stabilize the variance of measured values was introduced by Feudale et al. [5]. Forina et al. [6] compared the criteria that applied to select useful predictors in multiple calibration equations. However, the effect of the adequateness of the calibration models for measurement uncertainty was not mentioned.

In the content of the Appendix E-Statistical procedures, the EURACHEM/CITAC Guide [2], three formulas were proposed to calculate the uncertainty of predicted value X_{pred} due to variability in y with linear equation [2]. The uncertainty due to the errors in the reference values x_i and due to a constant unknown offsets were formulated in this literature. However, the effect of the nonlinearity case for calibration equation on uncertainty was still not be quantified. Therefore, the aim of the present study is to compare the effect of adequateness of the calibration model on the measurement uncertainty. The practical example included linear, polynomial, and power calibration equations of two types of thermometer.

Theory

In this study, the reference temperature environments, the known x_i values, were maintained by a portable temperature calibrator TC2000. The reading values, the response y_i, were taken from two types of thermometer. There are two methods to establish the calibration equations.

Established methods of calibration equation

1. The classical method

The response y_i was the function of standard values x_i,

$$y = f(x_i) \tag{1}$$

If y_i and x_i was assumed to be the linear relationship, then

$$y = b_0 + b_{1x} \tag{2}$$

As the new response, x_0, was measured, the true value is calculated as follows:

$$\hat{x} = \frac{\hat{y} - b_0}{b_1} \tag{3}$$

This procedure is called the "classical method". The calibration equation was established by ordinary least-square regression or nonlinearity regression technique. If y and x are related by a nonlinear or polynomial function, the estimated value ($\hat{x}$) belonging to a ($\hat{y}$) value can be calculated from an algebraic equation or computed using a numerical analysis technique.

2. The inverse method

In this method, the x_i is selected as the dependent variable and y_i is assumed as independent variable, the calibration equation is

$$x = f^1(y) \tag{4}$$

If y_i and x_i has the linear relationship,

$$x = c_0 + c_1 y_i \tag{5}$$

The $f^{-1}(y)$ can be a polynomial function or nonlinearity equation, such as:

$$x = c_0 + c_1 y + c_2 y^2 \tag{6}$$

Or a power equation:

$$x = d_0 y^{d_1} \tag{7}$$

The true value $\hat{x}$ can then be calculated directly by these equations. This approach is called the "inverse method".

The classical method has been mentioned in many textbooks of regression analysis. Krutchkoff [7] observed that the inverse method had smaller mean square errors than the classical method. After comparing the accuracy of predictions from the classical and inverse methods, Krutchkoff [7] concluded that the inverse method was better than the classical method regarding prediction. Centner et al. [8] proved this statement by Monte Carlo simulations and some practical cases. Their results indicated that the classical method gave more reliable predictive performance than the classical method. When comparing two approach calibration methods with small data sets, Tellinghuisen [9] had similar results. Crientschnig [10] confirmed that the inverse method had the better prediction ability than the classical method, regardless of the size of the data sets.

Criteria for model assessment

The relationships between reading values of thermometers and reference temperatures are calculated by statistical software. The standard error of the estimated value, s, was applied as the quantitative criterion.

$$s = \sqrt{\frac{\sum (y - \hat{y})^2}{n - 1}} \tag{8}$$

where y is the dependent variable, $\hat{y}$ is the predicted value of model, and n is the number of data.

The residual plots served as the qualitative criterion to evaluate the model. The relationship between the residuals of the model and the predicted values are plotted as the residual plots. As the model was adequateness, data distribution of residual plots should tend to be in a horizontal band centered on zero. If the residual plots indicated a clear pattern, the model could not be accepted.

Uncertainty of calibration equation due to variability in dependent variable

The standard uncertainty due to calibration equation is a Type A uncertainty. Three calibration equations are considered in this study.

The classical method

Linear equation

The linear regression calibration equation is:

$$y = b_0 + b_1 x \tag{9}$$

where y is the reading values of the thermometer and x is the reference temperature value.

The predicted value (x_{pred}) that calculated from the observed response (y_{obs}) has been discussed in detail [11, 12]:

$$x_{\text{pred}} = \frac{y_{\text{obs}} - b_0}{b_1} \tag{10}$$

The variance of x_{pred} is:

$$Var(x_{\text{pred}}) = \frac{s^2}{b_1^2}\left[\frac{1}{p} + \frac{1}{n} + \frac{(x_{\text{pred}} - \overline{x})^2}{\sum(x_i^2) - (\sum x_i)^2/n}\right] \tag{11}$$

where s is the standard deviation of calibration equation, p is the numbers of measurements for predictions, n is total number of measurement for calibration equation.

The standard deviation $s(y_c)$ for y value calculated from the fitted line for a new value of x,

$$s(y_c) = s\sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(x_{\text{pred}} - \overline{x})^2}{\sum(x_i^2) - \sum(x_i)^2/n}} \tag{12}$$

Combining Eqs. (11) and (12),

$$Var(x_{\text{pred}}) = \left[\frac{s(y_c)}{b_1}\right]^2 \tag{13}$$

then,

$$u(x_{\text{pred}}) = \frac{s(y_c)}{b_1} \tag{14}$$

The uncertainty of the predicted values obtained by the inverse method of the linear calibration equation could be computed by Eq. (14).

Polynomial equation

The form of polynomial calibration equation is:

$$y = c_0 + c_1 x + c_2 x^2 \tag{15}$$

The predicted value (x_{pred}) obtained from the observed response (y_{obs}) is calculated as:

$$X_{\text{pred}} \frac{-c_1}{2c_2} + \sqrt{\frac{c_1^2}{4c_2^2} - \frac{c_0}{c_2} + \frac{y_{\text{obs}}}{c_2}} \tag{16}$$

From the definition of uncertainty,

$$u(x_{\text{pred}}) = \frac{dx}{dy}u(y_i) \tag{17}$$

$$u(x_{\text{pred}}) = \frac{1}{2c_2}\frac{u(y_{obs})}{\sqrt{\frac{c_1^2}{4c_2^2} - \frac{c_0}{c_2} + \frac{y_{\text{obs}}}{c_2}}} \tag{18}$$

$u(y_{\text{obs}})$ was calculated by Eq. (12).

Power equation

The form of power calibration equation is:

$$y = d_0 x^{d_1} \tag{19}$$

The predicted value (x_{pred}) then could be calculated as:

$$x_{\text{pred}} = \left[\frac{y_{\text{obs}}}{d_0}\right]^{1/d_1} \tag{20}$$

From Eq. (17)

$$u(x_{\text{pred}}) = d_0^{(-1/d_1)} d_1^{-1} y^{((1-d_1)/d_1)} u(y_{\text{obs}}) \tag{21}$$

The inverse method

Linear equation

The form of linear regression model is:

$$x = e_0 + e_1 y \tag{22}$$

Polynomial equation

The form of polynomial equation is:

$$x = f_0 + f_1 y + f_2 y^2 \tag{23}$$

Power calibration equation

$$x = g_0 y^{g_1} \tag{24}$$

The uncertainty of x_{pred} is easy to be calculated by the following equation.

$$u(x) = s(x_c) = s\sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(y - \overline{y})^2}{\sum(y_i^2) - (\sum y_i)^2/n}} \tag{25}$$

Materials and methods

Thermometers

Two types of thermometer were applied in this study. One is the HH81A digital thermometer with k-type thermocouple (Omega Eng. Inc., CT, USA) and the other is Oakton TEMP

Table 1 Specification of two types of thermometer

	HH81A	Oakton TEMP 5
Sensing element	*K*-type thermocouple	TEMP 4 thermistor
Measuring range	–200 to 1,372°C	–40 to 125°C
Nonlinearity and repeatability	± 0.25°C	± 0.2°C
Resolution	0.1°C	0.1°C

5 meter (Oakton Instruments, IL, USA). The specifications of the two thermometers are listed in Table 1.

Reference temperature

The reference temperature for calibration was produced by TC2000 Temperature calibrator (Instutek AS, Skreppestad Naringspark, Norway). The temperature maintained ranged from –20 to 150°C. The expand uncertainty of this equipment was 0.04°C from the calibration certificate.

Calibration method

At the calibrating process, each thermometer was placed at the calibrated chamber of the TC2000. There were five replicates for the fixed temperature that ranged from 5 to 60°C. The calibrating interval of temperature was 5°C. There were 60 calibration data for each thermometer.

Statistics software

All regression analysis of data was executed by the SigmaStat 3.0 Ver (SPSS Inc., USA).

Results and discussions

Evaluation of calibration equation

The relationship between the reading values of HH81A thermometer and reference temperature is presented in Fig. 1.

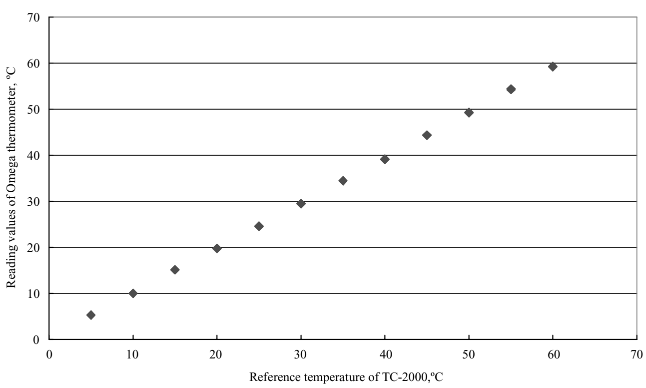
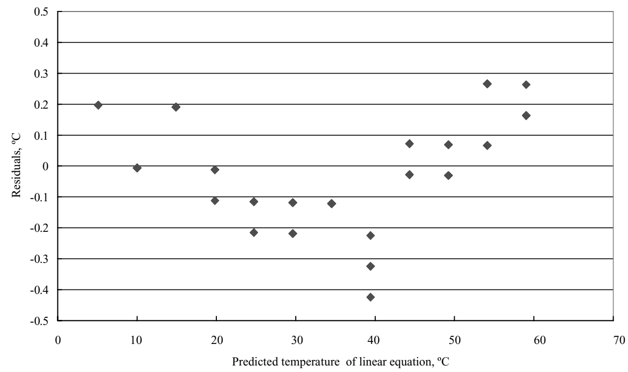
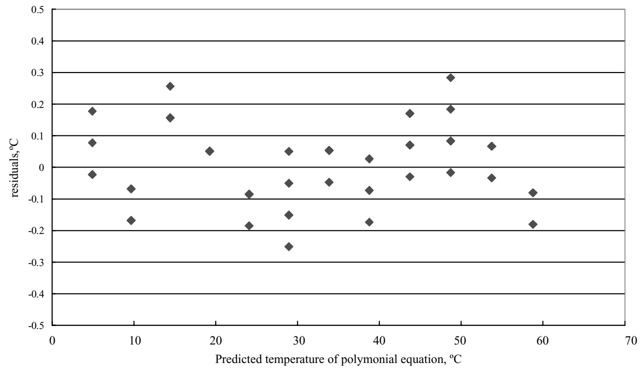


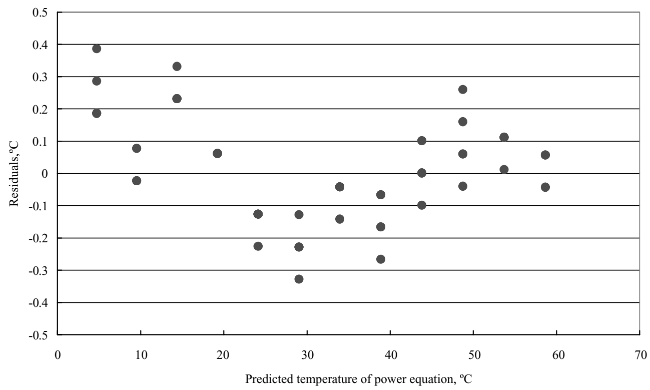
Fig. 1 Relationship between the reading values of HH81A thermometer and reference temperature.



a. Linear calibration equation



b. Polynomial calibration equation



c. Power calibration equation

Fig. 2 Residual plots of three calibration equations for HH81A thermometer

Three dimension-free quantities were defined as: $t_1 = T_1/°C$, $t_2/ = T_2/°C$ and $t_S = T_S/°C$. T_1 (°C) is the reading values of HH81A, T_2 (°C) is the reading value of TEMP 5 thermometer and T_S (°C) is the reference temperature. The results of regression analysis for three classical calibration equations are:

For linear equation,

$$t_1 = 0.19999 + 0.98061\, t_s, \quad s = 0.1697 \tag{26}$$

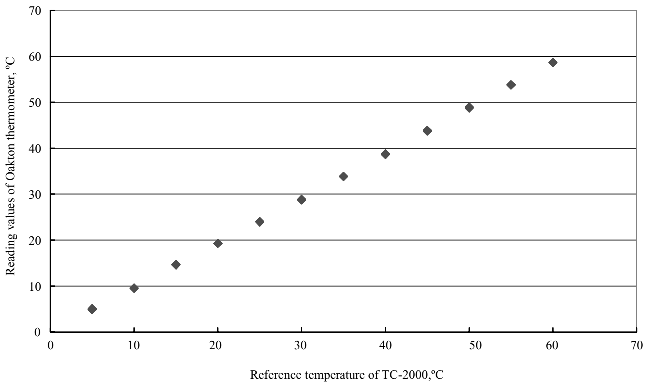


Fig. 3 Relationship between the reading values of HH81A thermometer and reference temperature. **a** Linear calibration equation. **b** Polynomial calibration equation. **c** Power calibration equation

For polynomial equation:

$$t_1 = 0.5718 + 0.9885\, t_s + 4.9031 \times 10^{-4}\, t_s^2,$$
$$s = 0.1081 \quad (27)$$

For power equation:

$$t_1 = 0.9972\, t_s\, 0.9969, \quad s = 0.1918 \quad (28)$$

The residual plots for the above equations are shown in Fig. 2. Only the polynomial equation indicated the uniform distribution of residual. The clear pattern of data distribution is easily found for the residual plots of the linear and power equations. The polynomial equation could serve as the adequate calibration equation.

The results of regression analysis for three inverse calibration equations of HH81A thermometer are:

$$t_s = -0.2008 + 1.0197 t_1, \quad s = 0.1730 \quad (29)$$

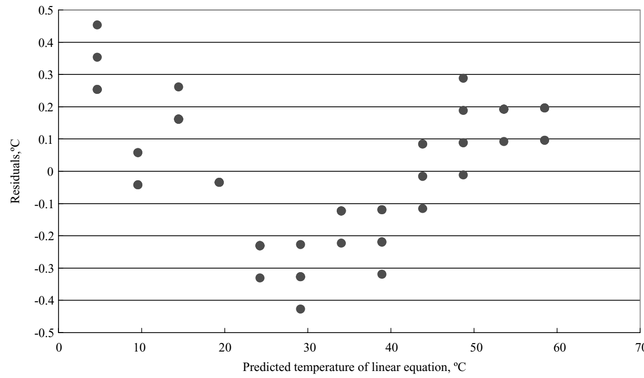
$$t_s = -0.5922 + 1.053\, t_1 - 5.1986 \times 10^{-4}\, t_1^2,$$
$$s = 0.1099 \quad (30)$$

$$t_s = 1.031\, t_1^{1.031}, \quad s = 0.1937 \quad (31)$$

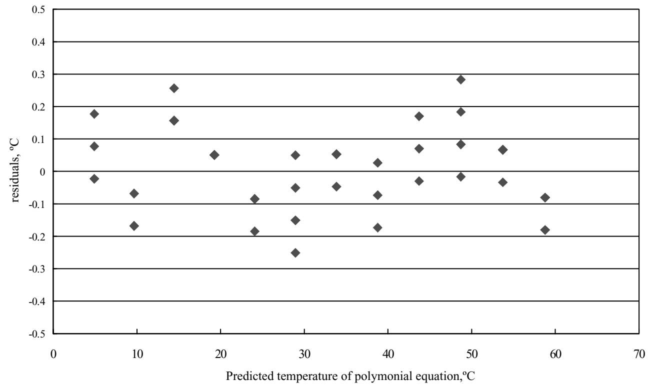
The relationship between the reading values of TEMP 5 thermometer and reference temperature is shown in Fig. 3. The results of regression analysis for three classical calibration equations are:

$$t_2 = 0.2501 + 0.9792\, t_s, \quad s = 0.2027 \quad (32)$$

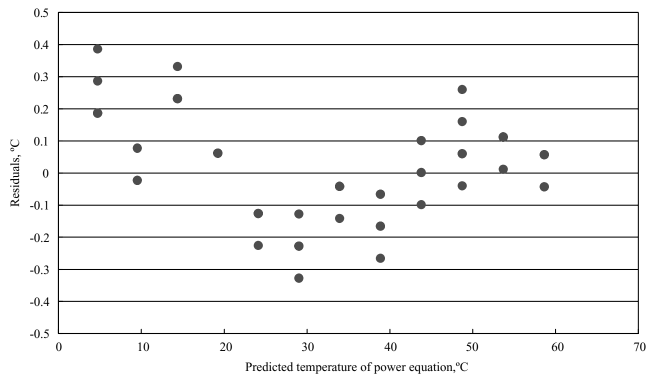
$$t_2 = 0.20773 + 0.9401\, t_s + 6.0360 \times 10^{-4}\, t_s^2,$$
$$s = 0.1230 \quad (33)$$



a. Linear calibration equation



b. Polynomial calibration equation



c. Power calibration equation

Fig. 4 Residual plots of three calibration equations for TEMP 5 thermometer

$$t_2 = 0.921\, t_s^{1.045}, \quad s = 0.1577 \quad (34)$$

The residual plots for the above equations are shown in Fig. 4. The polynomial equation could be viewed as an adequate calibration equation.

The regression analysis for three inverse calibration equation of TEMP 5 thermometer are:

$$t_s = 0.2598 + 1.0211\, t_2, \quad s = 0.2069 \quad (35)$$

Table 2 The predicted values and uncertainty of four representations for HH81A thermometer for three calibration equations. All values in °C

Calibration method	Regression equation	y_{res} 15°C x_{pred}	$u(x)$	25°C x_{pred}	$u(x)$	35°C x_{pred}	$u(x)$	45°C x_{pred}	$u(x)$
Classical	Linear	14.909	0.1757	24.715	0.1745	34.522	0.1734	44.328	0.1750
	Polynomial	14.913	0.1121	24.597	0.1120	34.379	0.1121	44.258	0.1118
	Power	14.833	0.1968	25.682	0.1970	34.519	0.965	44.348	0.1968
Inverse	Linear	15.094	0.1759	25.291	0.1747	35.488	0.1745	45.684	0.1753
	Polynomial	15.087	0.1176	25.413	0.1178	35.633	0.1200	45.746	0.1115
	Power	15.173	0.1970	25.329	0.1969	35.498	0.1961	45.6753	0.1963

$$t_s = -0.2055 + 1.0619\, t_2 - 6.4216 \times 10^{-4}\, t_2^2, \quad s = 0.1266 \tag{36}$$

$$t_s = 1.084\, t_2^{0.9858}, \quad s = 0.1619 \tag{37}$$

Sources of the uncertainty for thermometers

The uncertainty of measurement can be evaluated by "Type A" or "Type B" method [1]. The type A evaluation of uncertainty is the method by the statistical analysis of observations. The type B evaluation of uncertainty is the method by other information about the measurement.

There are several uncertainty sources. The uncertainties were calculated as follows:

The calibration equation

The uncertainty due to calibration is a Type A uncertainty. The uncertainty of three classical calibration equations of two types of thermometer could be calculated by Eqs. (11), (18), and (29). The uncertainties of three inverse calibration equations were calculated directly by Eq. (25). The results of uncertainty due to calibration equations are listed in Tables 2 and 3.

Comparing the uncertainty due to the calibration equations, the uncertainty of polynomial calibration is smaller than that linear and power calibration equation for two types of thermometer. The uncertainty of the linear calibration equation was better than that of the power calibration equation for the HH81A thermometer. However, the uncertainty of the power calibration equation was better than that of the linear calibration equation for the TEMP 5 thermometer. From the data distribution of residual plots, the polynomial equation is the only adequate model. This result confirmed the effect of the fitting-agreement of the calibration equation on the numeric values of measurement uncertainty.

Uncertainty of the reference standard

The uncertainty of the TC2000 calibrator, U_{ref}, was 0.04°C. The numeric value was an expanded uncertainty. The probability distribution for reference standard was assumed as normal distribution, the uncertainty of the reference standard was:

$$u_{ref} = U_{ref}/2 \tag{38}$$

Uncertainty due to nonlinearity and repeatability

The derivation U_{non} due to nonlinearity and repeatability is specified by manufacture's specification. The variation response for this error is assumed as a rectangular distribution. The uncertainty, u_{non}, is calculated as

$$u_{\mathrm{non}} = \pm \frac{U_{\mathrm{non}}}{2\sqrt{3}} \tag{39}$$

Uncertainty due to resolution

The uncertainty due to resolution is assumed as a rectangular distribution. It is considered as $\pm 1/2$ of the scale value

Table 3 The predicted values and uncertainty of four representations for TEMP 5 thermometer for three calibration equations. All values in °C

Calibration method	Regression equation	y_{res} 15°C x_{pred}	$u(x)$	25°C x_{pred}	$u(x)$	35°C x_{pred}	$u(x)$	45°C x_{pred}	$u(x)$
Classical	Linear	15.576	0.2059	25.787	0.2046	35.997	0.2044	46.208	0.2054
	Polynomial	14.444	0.1251	24.085	0.1251	33.847	0.1252	44.729	0.1248
	Power	14.367	0.1580	24.125	0.1583	33.940	0.1555	43.797	0.1540
Inverse	Linear	14.439	0.2061	24.231	0.2047	34.023	0.2044	44.815	0.2052
	Polynomial	15.578	0.1287	25.940	0.1287	36.174	0.1289	46.279	0.1283
	Power	15.647	0.1646	25.890	0.1645	36.072	0.1639	46.211	0.1640

Table 4 The type B uncertainty analysis for HH81A thermometer

Description	Estimate value	Standard uncertainty u(x)	Probability distribution
Reference standard, U_{ref}	±0.04°C	0.020°C	Normal
Nonlinearity and Repeatability, U_{non}	±0.25°C	0.072°C	Rectangular
Resolution, U_{res}	±0.1°C	0.029°C	Rectangular

Table 5 The type B uncertainty analysis for TEMP 5 thermometer

Description	Estimate value	Standard uncertainty u(x)	Probability distribution
Reference standard, U_{ref}	±0.04°C	0.020°C	Normal
Nonlinearity and Repeatability, U_{non}	±0.20°C	0.057°C	Rectangular
Resolution, U_{res}	±0.1°C	0.029°C	Rectangular

of the display. The uncertainty due to resolution (u_{res}) is estimated as following:

$$u_{res} = \pm \frac{U_{res}}{2\sqrt{3}} \tag{40}$$

The uncertainty due to the reference standard, nonlinearity and repeatability, and resolution are classified as Type B uncertainty. The results of Type B uncertainty for the two types of thermometer are listed in Tables 4 and 5.

The combined standard uncertainty

The combined standard uncertainty (u_c) can be estimated by as follows:

$$\begin{aligned} u_c &= \sqrt{\sum u_i^2} \\ &= \sqrt{u_{X_{pred}}^2 + u_{ref}^2 + u_{non}^2 + u_{res}^2} \end{aligned} \tag{41}$$

The u_c values for the two types of thermometer with classical and inverse calibration equation at four observations are listed in Table 6.

According to Eq. (41), the values of u_c are calculated at 15, 25, 35 and 45°C of the observed temperature. They are found to be 0.1931, 0.1920, 0.1910 and 0.1925°C for the HH81A thermometer using the linear classical calibration equation, respectively. For the polynomial calibration equation, the combined standard uncertainty evaluated at 15, 25, 35 and 45°C were 0.1378, 0.1377, 0.1378 and 0.1376°C, respectively. The combined standard uncertainties evaluated at the same four temperatures by power calibration equation were 0.2116, 0.2103, 0.2092 and 0.2108°C, respectively. The polynomial calibration equation had the smallest combined uncertainty of the three calibration equations. The linear and power calibration equations are inadequate model for the display of residual plots. This result indicated that the inadequate calibration equation could increase the uncertainty significantly. A similar result was also found for the inverse calibration equation. Comparing the combined standard uncertainty of the polynomial calibration equations to the classical model and inverse model for observation values of 15, 25, 35 and 45°C, both sets of data did not have the significant difference for HH81A thermometer.

The values of u_c obtained at 15, 25, 35 and 45°C of the observed temperature for the TEMP 5 thermometer had the similar results. The u_c values of the polynomial calibration equation are smaller than that of linear and power calibration equations for both classical and inverse equations. No significant difference could be found between the classical methods and the inverse method.

The uncertainty arising from the inadequate calibration equation was not mentioned in the EURACHEM/CITAC Guide quantifying uncertainty in analytical measurement [2]. The methods of calibrating and comparing of *u(x)* due to the addition variation of inadequate calibration

Table 6 The combined standard uncertainty for two thermometers. All values in °C

Thermometer	Calibration method	Regression equation	Observations 15°C	25°C	35°C	45°C
HH81A	Classical	Linear	0.1931	0.1920	0.1910	0.1925
		Polynomial	0.1378	0.1377	0.1378	0.1376
		Power	0.2115	0.2127	0.2122	0.2125
	Inverse	Linear	0.1933	0.1922	0.1920	0.1928
		Polynomial	0.1423	0.1425	0.1443	0.1373
		Power	0.2127	0.2126	0.2118	0.2120
TEMP5	Classical	Linear	0.2165	0.2153	0.2151	0.2161
		Polynomial	0.1419	0.1419	0.1420	0.1417
		Power	0.1716	0.1719	0.1693	0.1679
	Inverse	Linear	0.2167	0.2154	0.2151	0.2159
		Polynomial	0.1451	0.1451	0.1453	0.1447
		Power	0.1777	0.1776	0.1771	0.1772

equation was proposed in this study. The adding variation of inadequate equation is found as the main source of uncertainty for two types of thermometer. There was no significant difference of the combined uncertainty between the classical and inverse methods. However, the calculation procedure of the inverse method was simpler and easier than that of the classical method.

Conclusion

The sources of uncertainty for two types of thermometer were evaluated. These sources include predicted values of calibration equation, nonlinearity and repeatability, reference source, and resolution source. The effect of the adequateness of the calibration equations on the uncertainty was investigated. The uncertainty analysis shows that the predicted uncertainly is the main source for combined uncertainty. No significant difference of the uncertainty for two types of thermometer was found between the classical method and the inverse method. For both thermometers, the adding variation of inadequate calibrations equation is found as the main source of uncertainty.

References

1. ISO (1995) Guide to the expression of uncertainty in measurement. ISO, Geneva
2. EURACHEM/CITAC (2001) Quantifying uncertainty in analytical measurement, 2nd edn., Final Draft April 2000, EURACHEM: 11–13. EURACHEM/CITAC http://www.eurachem.ul.pt/guides/QUAM2001-1.pdf
3. Geladi P, Hadjiiski L, Hopke P (1999) Chemometrics and Intelligent Laboratory Systems 47:165–173
4. Geladi P (2002) Chemometrics and Intelligent Laboratory Systems 60:211–224
5. Feudale RN, Woody NA, Tan H, Myles AJ, Brown SD, Ferre J (2002) Chemometrics and Intelligent Laboratory Systems 64:181–192
6. Forina M, Lanteri S, Oliveros MCC, Millan CP (2004) Anal Bioabal Chem 380:397–418
7. Krutchkoff RG (1967) Technometrics 9:425–439
8. Centner V, Massart DL, de Jong S (1998) Fresenius J Anal Chem 361:2–9
9. Tellinghuisen J (2000) Fresenius J Anal Chem 368:585–588
10. Grientschnig D (2000) Fresenius J Anal Chem 367:497–498
11. Bruggemann L, Wennrich R (2002) Accred Qual Assur 7:269–273
12. Heydorn K, Anglov T (2002) Accred Qual Assur 7:153–158