Calibration and self-validation of thermistors for high-precision temperature measurements

Steffen Rudtsch*, Christoph von Rohden
Physikalisch-Technische Bundesanstalt (PTB), Braunschweig und Berlin, Germany
*corresponding author. Tel.: +49 3034817650; fax.: +493034817504; E-mail address: steffen.rudtsch@ptb.de.

ABSTRACT

In this paper we discuss influencing variables affecting the uncertainty of high-precision temperature measurements (u<1 mK) by means of NTC thermistors. These are proper instrument settings, a suitable choice (distribution) of calibration temperatures in due consideration of uncertainties, self heating and the number of parameters in the calibration equation. Within this work we used 4 wire measurements to eliminate the influence of lead resistances, switched dc current to reduce errors by thermoelectric effects and amplifier offsets, a reference resistor with a nominal value close to the thermometer resistance to maximize the resolution and a maximum current consistent with the input voltage range and self heating of the thermistor.
We present results of high-precision calibrations of a so called super-stable thermistor and demonstrate the influence of changes of the calibration equation on the interpolation error. Our results confirm previous findings that the number of parameters in the interpolation equation can have a considerable influence on the interpolation error. It was confirmed that the Steinhart-Hart equation shows a poor performance and should be replaced by the more suitable models recommended in [1]. For the quantification of the long term stability of a calibration we recommend repeated single-point validations at the triple-point of water. If these are supplemented by measurements at the gallium fixed-point possible changes of the curvature of the characteristics can be detected.

1. Introduction

There is an increasing need for temperature measurements with uncertainties on a millikelvin-level in the temperature range between -20 °C and +50 °C. This is related to requirements in various fields such as ocean temperature measurements, air and artifact temperature monitoring in dimensional metrology laboratories but also to specific industrial applications in precision manufacturing, optics and semiconductor production. Compared with metrology-grade platinum resistance thermometers, thermistors have a higher sensitivity (up to ten times), are less sensitive to mechanical shock or vibrations and can be manufactured with smaller diameter. For so called ultra-stable thermistors, manufacturers claim accuracies better that 1 mK and drift rates less than 2 mK/year. This requires appropriate standards and techniques which can be used to (re-)calibrate sensors and to validate the uncertainty claims.
In the following we discuss methods for the quantification of the dominating uncertainty contributions and optimum instrument settings. Due to the strong non-linearity of the thermistor characteristics, the calibration equation should follow a suitable mathematical model with a specific number of individual parameters [1]. As a consequence high-precision applications with thermistors require a calibration at a minimum number of 4-5 well distributed temperatures. These should always include the maximum and minimum application temperatures.
The calibration techniques are the so called comparison method and fixed-point calibrations. In the comparison method a calibrated Standard Platinum Resistance Thermometer (SPRT) is used as a reference for the calibration of a thermistor in a stirred liquid bath with excellent temperature stability and homogeneity. By means of this method typical uncertainties of (2-3) mK are achieved. For thermometer calibrations at the triple point of water (0.01 °C) uncertainties below 0.1 mK are state of the art, at the Ga- (29.7646 °C) and Hg-fixed points (-38.8344 °C) about 0.25 mK are possible. Therefore, a thermistor calibration with smallest possible uncertainties requires the combination of both techniques, the comparison method for the characterization of the curvature and

[1] *Certain commercial equipment, instruments or sensors are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by PTB, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.*

complementary measurements with lower uncertainties at selected fixed-points. Due to the required effort, repeated “calibrations” are in practice often carried out at only one or two temperatures.
A single-point test at only one fixed-point temperature is referred to as “validation”. Repeated single-point validations allow a quantification of the drift with better accuracy than calibrations or validations by means of the comparison method. Although a drift of resistance based temperature sensors is mostly a shift of the calibration function (offset), some physical processes such as the so called poisoning by impurities can change the curvature of the characteristics. Therefore, an additional validation at another fixed-point temperature can indicate such variations and provides supplementary information about the mechanism of changes of the calibration results.

2. Experimental

In this work we exemplarily present calibration results for a MEAS type 46016 thermistor[1] with a nominal resistance value of about 10 kΩ at 25 °C. The sensor was assembled in a hermetically sealed stainless steel housing with 4-wire PTFE insulated cables. By investigations of other sensors of the same type it was checked whether the calibrated one showed a typical behavior. For the resistance measurements of the thermistor and Standard Platinum Resistance Thermometer (SPRT) an ISOTECH instrument type microK 70[1] was used. The microK uses a four-wire technique to eliminate lead resistances and a 10 Hz bipolar switched dc current to eliminate errors associated with thermoelectric effects and amplifier offsets. The calibrations were carried out in the resistance ratio mode by direct comparison with thermostated Wilkins-type standard resistors. Typical measurement currents were 1 mA for SPRTs and 10 µA for thermistors. Different currents have been applied to each sensor to allow a correction to zero self heating.
The determination of the characteristics of the thermistor is based on a calibration by means of the comparison method. For this purpose a calibrated SPRT was used as a reference thermometer in a thermostated and well circulated water bath (55 l) with a temperature stability and homogeneity of typically 0.5 mK. Two series of calibration were carried out (May 2014 and February 2015) in the temperature range between 5 °C and 60 °C. Between the calibrations the sensor was stored at room temperature. In order to reduce the uncertainties the results were validated by additional calibrations at the triple point of water and the Ga fixed point.

3. Results and discussion

3.1 Optimum instrument settings

In a first step the instrument settings were optimized. These improvements included four wire resistance measurements, specific shielding of cables, a suitable choice of integration (measurement) time but most important a proper selection of measurement current and reference resistor. Previous own investigations by means of a Hamon-type Resistance Bridge Calibrator have shown that an improper choice of the range used for the resistance ratio measurement can deteriorate the linearity by more than one order of magnitude. We found that for a microK-type of instrument, optimum linearity (about 0.04 ppm) is achieved in the resistance ratio range between 0.2 and 1.2. Because the microK measures ratios of voltage drops across the reference resistor and the unknown resistor by means of a specific substitution technique, a superior stability at unity ratio was expected. To maximise the resolution it is advisable to use a reference resistor close to the maximum resistance of the thermistor. The maximum current should be consistent with the input voltage range (125 mV or 500 mV) and the self-heating of the thermistor.
This was supported by the results of noise measurements. In Fig. 1 the noise for a 10 kΩ resistor (Vishay type VH102ZT) is exemplarily shown for two different setups, first (gray) with the internal 400 Ω reference resistor of the instrument and second (blue) with a 10 kΩ external Wilkins-type standard resistor as a reference.

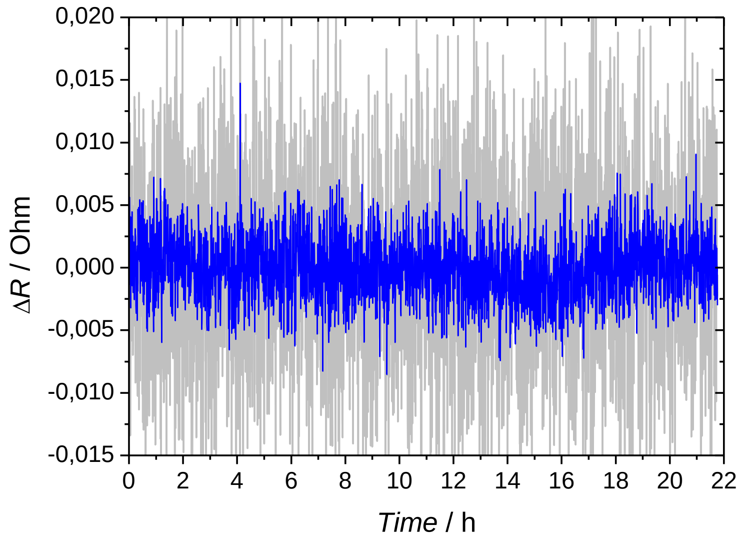

Figure 1 Noise for the measurement of a 10 kΩ reference resistor (*I*=10 µA)
blue: with an external 10 kΩ Wilkins-type standard resistor
gray: with the internal 400 Ω reference resistor

The results demonstrate that by using a reference resistor of a similar nominal value the standard deviation is reduced by a factor of 3 (from 7.5 mΩ to 2.5 mΩ). For a thermistor with a resistance value of 10 kΩ at 25 °C this corresponds to a decrease in the temperature noise from 17 µK to 6 µK. With a suitable shielding these small noise levels are also achieved using thermistors in fixed-point cells (Fig. 2).

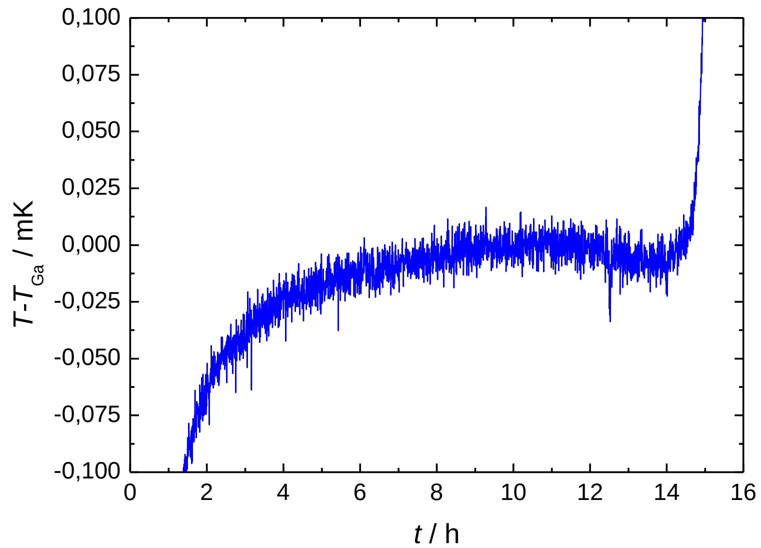

Figure 2 Typical melting curve of a commercial Ga-fixed-point cell, measured with a thermistor

Although the small variation of the fixed-point temperature after a sufficient run-in time of about 4 hours indicates stability better than ±30 µK the pressure dependence of the fixed-point temperature and other contributions lead to typical uncertainties of about 250 µK for commercially available Ga fixed-point cells. Further improvements with uncertainties below 100 µK are possible with well characterized pressure controlled Ga fixed-point cells and specific preparation methods for the inner phase boundary.
Furthermore, high-precision temperature measurements with resistance thermometers always require the consideration of the self heating. It depends on the power (electrical resistance and

measuring current), internal design of the sensor and the heat transfer conditions between sensor and the surrounding medium.
Figure 3 exemplarily shows the self heating of the investigated thermistor at the Ga fixed point (29.7646 °C) determined with currents between 5 µA and 10 µA. Since calibration and application of resistance thermometers are mostly carried out at different heat transfer conditions, an extrapolation to zero self heating is necessary to transfer smallest possible calibration uncertainties to application related uncertainties.

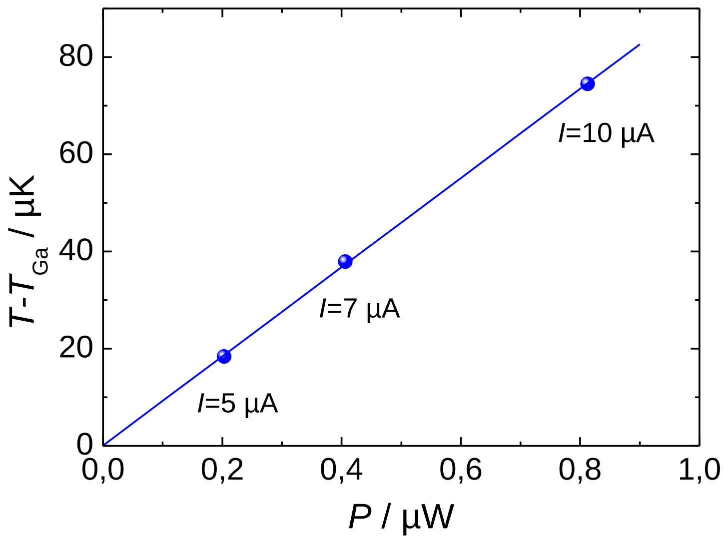

Figure 3 Self heating of the thermistor in the Ga fixed-point cell

Whereas the self heating of 25 Ohm SPRTs operated with a current of typically 1 mA amounts to about 2 mK (in water), the self-heating of the thermistor investigated within this work at a current of 10 µA is more than one order of magnitude smaller.
Due to the non-linear characteristics of thermistors a measurement with the same current in the whole temperature range would result in a considerable change (variation) of the self heating.
As an example, for a thermistor of this type operated between 0 °C and 30 °C this causes a change in self heating by a factor of 4. Therefore, it is necessary either to consider the temperature dependence of the self heating or to reduce the measurement current with increasing thermistor resistance.

3.2 Thermistor Calibration

Since the 1950s several investigations [2-8] were carried out to find the most suitable relationship between electrical resistance and temperature for NTC thermistors. Due to the complex nature of the physical processes inside of the sensing element (mixture of metal oxides) an equation derived from first principles is not available.
Theoretical and experimental investigations have shown that the overall resistance-temperature relation is well approximated by

$$R_T = R_0\, e^{\beta\left(\frac{1}{T}-\frac{1}{T_0}\right)}. \tag{1}$$

T_0 is a convenient reference temperature, R_0 the corresponding resistance and β a material property of the thermistor with typical values between 2000 K and 6000 K [1]. In the following R_0 and T_0 were chosen on the basis of the resistor R_S (about 10 kΩ) which was used as the reference (standard) resistor for the resistance ratio measurement.
Calibration equations are derived by series expansions of (1):

$$\frac{1}{T} = \sum_{i=0}^{n} c_i \left[\ln\left(\frac{R_T}{R_S}\right)\right]^i \qquad (2)$$

The order is commonly chosen to $n \leq 4$. This includes the so called Basic Equation with $n=1$, and the widely used Steinhart-Hart equation [2] which omits the second order term, i.e. $n=3$ and $c_2=0$. In the following we compare the influence of a suitable choice of parameters on the quality of the fit (residuals) for high-precision measurements by means of the comparison method.

Due to the mathematical model consisting of up to 5 unknown parameters, at least five different calibration temperatures are required. It is very important that the calibration temperatures cover the whole temperature range, in particular the lowest and highest temperature. This is because the total propagated uncertainty is flat over an interpolation range, but rises very steeply where temperature is extrapolated beyond the calibration range [1]. Because there are only 2-3 readily available fixed points (Hg, TPW, Ga) in this range, thermistors are usually calibrated by comparison with an SPRT in a liquid bath. Within this work the temperature in the water bath has been preselected in (5 to 10) K steps between 5 °C and 60 °C. From the continuous data records, two to three pairs of values for R_T/R_S and temperature have been saved at each pre-selection, each of them as an average of 10 or more single readings within at least 1.5 min (Table 1).

Table 1. Measured data: Bath temperature T and resistance ratio R_T/R_S (test thermistor R_T and reference resistor R_S = 10001.65 Ω). Upper part: May 2014, lower part: February 2015

T / °C	R_T/R_S	T / °C	R_T/R_S	T / °C	R_T/R_S
5.0644	2.528758	19.9862	1.248332	34.9522	0.653541
5.0020	2.536562	19.8933	1.253592	35.0025	0.652198
4.9939	2.537604	20.0174	1.246570	45.3601	0.430282
10.1081	1.977502	24.9856	0.999239	45.0092	0.436225
9.9604	1.991586	24.8933	1.003293	44.9030	0.438038
10.0038	1.987436	25.0171	0.997861	55.2567	0.295619
15.0808	1.563295	29.7400	0.813533	54.9280	0.299233
14.9729	1.571180	29.6508	0.816633	54.9966	0.298474
15.0000	1.569187	29.7712	0.812447	60.0836	0.247962
4.9943	2.537485	19.9867	1.248269	44.9905	0.436526
9.7965	2.007273	24.9805	0.999413	44.9879	0.436568
9.7916	2.007747	24.9846	0.999235	54.9898	0.298537
14.8867	1.577444	29.9872	0.804964	54.9851	0.298587
14.8912	1.577119	34.9872	0.652595	59.8922	0.249662
19.9844	1.248398	34.9886	0.652560		

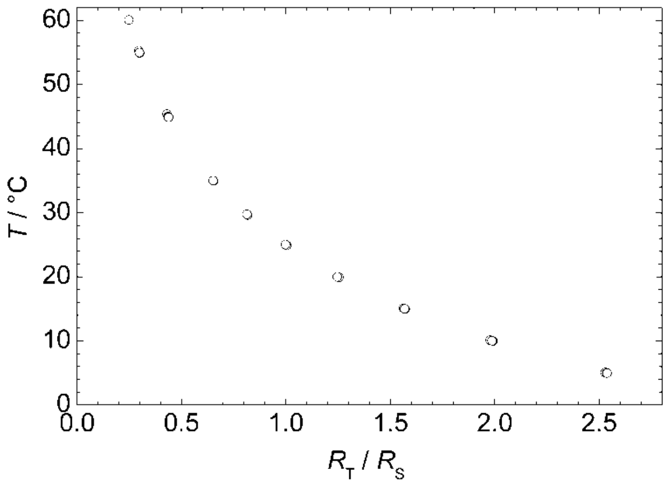

Figure 4. Calibration results and characteristics for a MEAS type 46013 thermistor calibrated in a water bath.

By means of our data we illustrate the quality of representations according to Eq. 2. Considering different polynomial orders n and non-zero coefficients c_i in least squares fits, we show the respective variation of the fitting uncertainty by validating the temperature residuals. Fig. 5 shows exemplary the least squares fit to the data (May 2014) according to the polynomial in Eq. (2) with n=4.

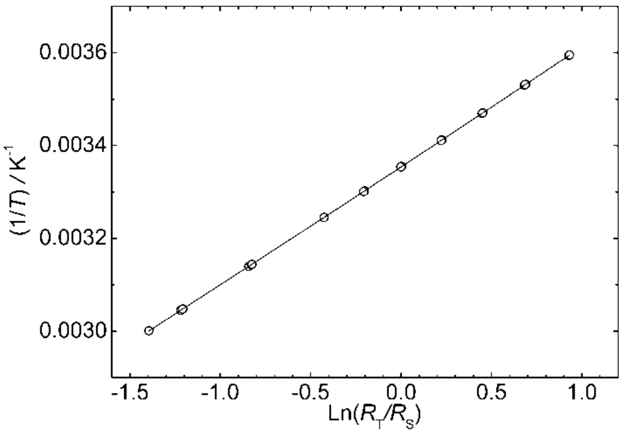

Figure 5. Least squares fit (line) to data (circles) according to Eq. (2) with n=4 and $c_i \neq 0$.

Usually, the quality of the calibration function increases with increasing polynomial order. The Steinhart-Hart equation which is recommended by many manufacturers however results in a poor representation of the thermistor characteristics in comparison to the complete equation with n=3 (compare panels a) and c) in Fig. 6) and even with n=2 (panel b)). Using a higher order than n=3 (panel d)) does not result in a decided improvement of the fit. That is, for our example we conclude that Eq. (2) with n=3 or n=4 including all terms would give an adequate calibration function, supported by the quasi-random distribution of the residuals. For $n \leqq 2$ clear residual pattern are present.

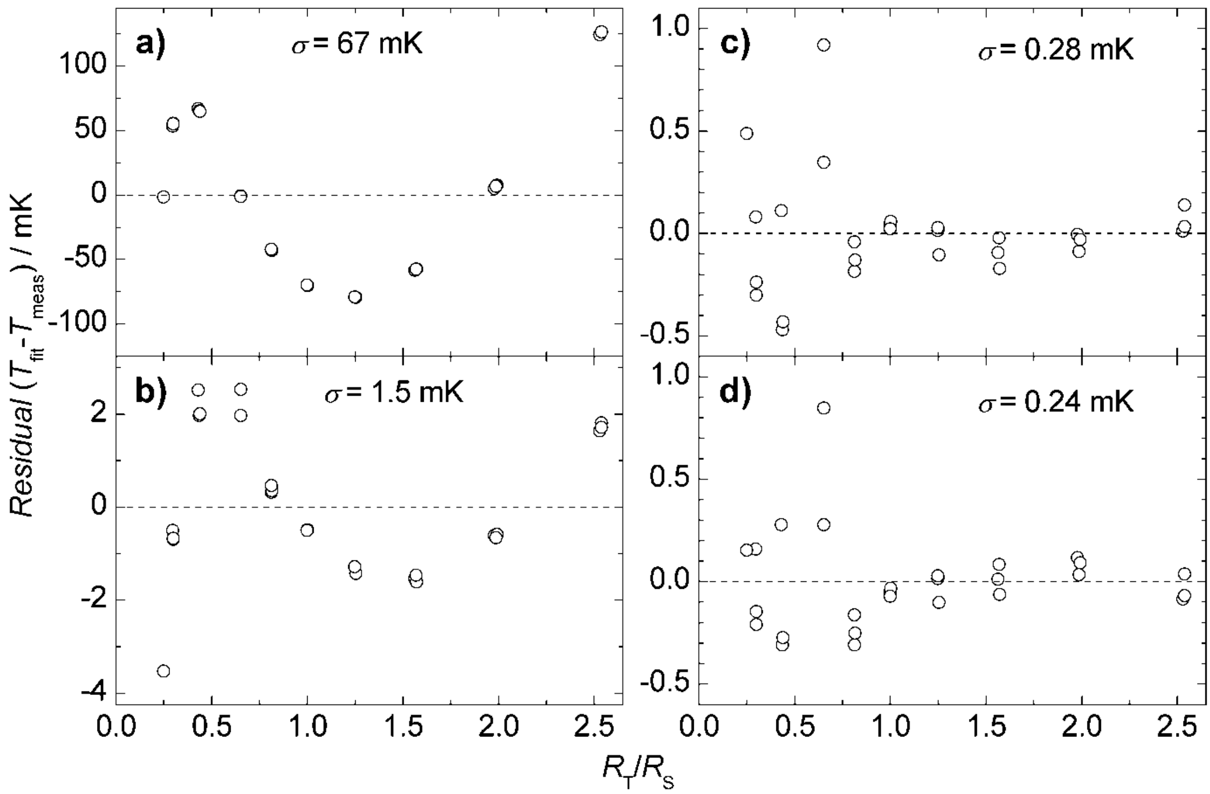

Figure 6. Residuals and standard deviations for the data (May 2014) shown in Fig. 5. Panel a): n=3, c_2=0 (Steinhart-Hart); panel b): n=2; panel c): n=3; panel d): n=4.

To account for the long-term stability of the thermistor and to check possible changes in the curvature of the characteristics, we conducted two calibration cycles three-fourths of a year apart (May 2014 and February 2015, upper and lower part of Table 1), using identical instrumentation, instrument settings, and SPRTs. Table 2 lists the fit coefficients for both calibration cycles.

Table 2. Polynomial coefficients c_i (n=4) for two calibration cycles according to Eq. (2).

i	*May 2014*	*Feb 2015*
0	$3.3543740\cdot10^{-3}$	$3.3543842\cdot10^{-3}$
1	$2.5651814\cdot10^{-4}$	$2.5651728\cdot10^{-4}$
2	$2.25341\cdot10^{-6}$	$2.24602\cdot10^{-6}$
3	$6.64\cdot10^{-8}$	$6.66\cdot10^{-8}$
4	$8.01\cdot10^{-9}$	$1.28\cdot10^{-8}$
σ	0.24 mK	0.12 mK

The curve in Fig. 7 shows the difference of the fitted characteristics. From the zero-order coefficients c_0, a rough measure for a possible overall thermistor drift can be deduced, which is related to the ratio (R_T/R_S)=1, i.e. to a thermistor resistance and temperature close to the nominal value of 10 kΩ at 25 °C. In that sense, the apparent drift would amount to -0.94 mK, indicated with the distance between the constant dashed and solid lines in Fig. 7. With calibration uncertainties of about 1 mK for the comparison method (Table 3) it is not possible to quantify a drift of the thermistor during this time.

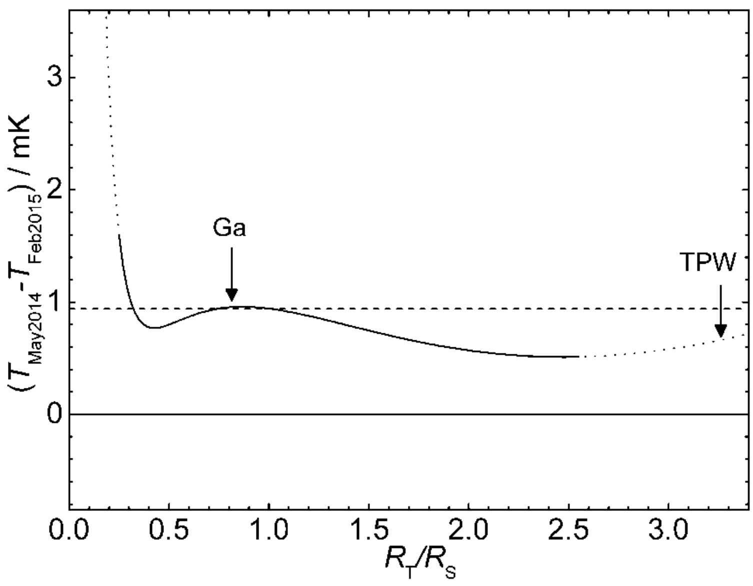

Figure 7. Difference between the fitted characteristics for the thermistor calibrated during May 2014 and February 2015, respectively. The line is extended as dots for the temperatures not covered by the comparison measurements in the liquid bath. Arrows: Resistance ratio positions of the gallium fixed point and the triple point of water. Dashed line: offset (apparent thermistor drift) of −0.94 mK, calculated for a resistance of 10 kΩ (R_T/R_S=1), corresponding to a temperature of 25 °C.

For the thermistor investigated here we can also state that the higher order changes of the characteristics are at most of the same order as the estimated drift. However they are hardly significant within the standard deviations of the polynomial fits (0.24 mK and 0.12 mK with n=4, for the first and the second calibration cycle, respectively).

From the comparison measurements, the resistance ratios for the temperatures of the fixed points of gallium and the triple point of water can formally be extracted from the fit. Changes of this ratio may indicate higher order changes of the characteristics (curvature). For the comparison method the ratios were R_{TPW}/R_{Ga}=(4.01266±0.00052) and (4.01269±0.00064), respectively, indicating no significant change as stated above within the uncertainties. It should be noted that the lowest calibration temperature for the comparison method was about 5 K above the temperature of the triple point of water. Therefore, the thermistor resistance at the triple point of water was derived from the fits by extrapolation. The corresponding uncertainty was estimated to be 2 mK.

Generally, the fixed point temperatures of the gallium point and the triple point of water can be realized with smaller uncertainties of 250 µK and 100 µK, respectively, or better. With measurements in a Ga fixed-point cell and in a triple point of water cell we determined the ratio for the same thermistor, yielding R_{TPW}/R_{Ga}=(4.01228±0.00005). This value is consistent with the ratios from the fits. Repeated validations at the triple point of water and the Ga fixed point can therefore provide both, a more accurate quantification of the drift and an earlier detection of changes in the curvature. The resulting uncertainties are about one order of magnitude smaller than with the comparison method (Table 3). Due to the increasing sensitivity of NTC-thermistors at low temperatures and smaller realization uncertainties, drift investigations should be preferentially carried out at the triple point of water.

Table 3. Attainable uncertainties for a calibration of a high-accuracy thermistor in the temperature range between 0 °C and 60 °C.

Uncertainty contributions (k=1)	0.01 °C Triple point of water	5 °C Comparison method	29.7646 °C Ga fixed-point	60 °C Comparison method
Resistance measurement	0.02 mK	0.02 mK	0.02 mK	0.02 mK
Fixed point temperature	0.05 mK	0.5 mK	0.13 mK	1.0 mK

resp. SPRT calibration				
Calibration bath, stability and spatial non-uniformity	0.00 mK	0.3 mK	0.00 mK	0.3 mK
Self-Heating	0.03 mK	0.03 mK	0.03 mK	0.03 mK
Stray thermal influences	0.01 mK	0.05 mK	0.01 mK	0.05 mK
Total (*k*=1)	**0.06 mK**	**0.6 mK**	**0.13 mK**	**1.1 mK**

If the interpolation function is based on calibrations carried out by means of the comparison method and a least-squares fit of Equation (2) the total propagated uncertainty will be flat over the interpolation range [1]. When additional fixed-point calibrations are included the propagated uncertainty will have local minima at the fixed-point temperatures. A consideration of the smaller uncertainties of fixed-point calibrations is possible by weighted least-squares fitting.

4. Conclusions

It has been demonstrated that with an NTC thermistor in a temperature range between 0 °C and 60 °C, similar uncertainties can be achieved as with Standard Platinum Resistance Thermometers. But, sub-millikelvin uncertainties require specific provisions regarding instrument settings, a suitable number and selection (distribution) of calibration temperatures by a combination of fixed-point calibrations with calibrations by means of the comparison method and a proper choice of the calibration equation with a sufficient number of parameters.

Optimum instrument settings require an analysis and measures to minimize all significant sources of uncertainty. Within this work we used 4 wire measurements to eliminate the influence of lead resistances, switched dc current to reduce errors by thermoelectric effects and amplifier offsets, a reference resistor with a nominal value close to the thermometer resistance to maximize the resolution and a maximum current consistent with the input voltage range and self heating of the thermistor.

Our results support previous findings of other authors that the number of parameters can have a considerable influence on the interpolation error.

It was confirmed that the Steinhart-Hart equation shows a poor performance and should be replaced by the more suitable models recommended in [1]. In contrast to recommendations of some other authors we can’t confirm that a further increase from 4 to 5 parameters significantly improves the quality of the fit. Additional fixed-point calibrations have two advantages, significantly reduced (propagated) uncertainties near to these fixed-point temperatures and superior drift determination.

For the quantification of the long term stability of a calibration we recommend repeated single-point validations at the triple-point of water. If these are supplemented by measurements at the gallium fixed-point possible changes of the curvature of the characteristics can be detected. Based on such intermediate validation measurements suitable re-calibration intervals can be determined.

Acknowledgment

This research was undertaken within the project EMRP ENV05. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

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