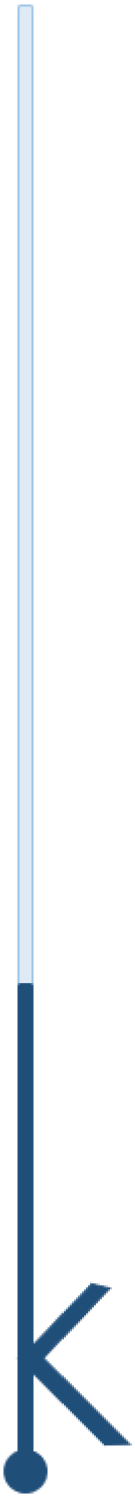

Bureau International des Poids et Mesures

Guide to Secondary Thermometry

Thermocouple Thermometry: 2. Calibration

Consultative Committee for Thermometry
under the auspices of the
International Committee for Weights and Measures

Thermocouple Thermometry: 2. Calibration

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Guide on Secondary Thermometry

Thermocouple Thermometry Part 2: Calibration

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ABSTRACT

The Guides on Secondary Thermometry are prepared by the Consultative Committee for Thermometry to provide advice on measurement practice and making temperature measurements traceable to the International Temperature Scale of 1990. This guide is the second of two collating information and advice on thermocouple thermometry. Part I focused on general usage of thermocouples and the causes of measurement error. This guide, Part II, focuses on calibration including reference thermocouples, calibration methods, calibration equations, the analysis, assessment and propagation of uncertainty, and reporting. Of necessity, it is more mathematical than Part I, but it builds on and should be read in conjunction with Part I.

1. Introduction

Thermocouples are the most used of all thermometers, but amongst the least frequently calibrated. As explained in Part I of this guide, the act of calibrating a thermocouple and exposing it to different temperatures may cause changes in the thermoelectric state of the wires that render the calibration meaningless. However, there are applications where calibration is essential, there are methods for minimising the compromising effects, and there are thermocouple types that are better behaved than others. This guide provides advice on procedures for the effective calibration of thermocouples.

A reference thermocouple is one used to calibrate other thermometers, usually other thermocouples. To be useful as a reference, a thermocouple must

- be of a type and construction with a history of satisfactory use under the expected conditions,
- have a satisfactory and quantified thermoelectric homogeneity,
- have a well-defined thermoelectric state to which it can be readily restored,
- have a well-characterised response to temperature, including the uncertainties in temperatures inferred using that response.

One of the key differences between reference and working thermocouples is that reference thermocouples are used, and must be calibrated, over a range of temperatures. In contrast, working thermometers are often used in a fixed location at a single temperature. The need for reference thermocouples to operate over a range of temperatures, in a range of different apparatus, with different immersion conditions, means that thermocouples exhibiting low inhomogeneity and low drift are required. For the most part, these requirements restrict reference thermocouples to noble metal thermocouples, especially Au/Pt, Pt/Pd, and the Pt/Rh alloy Types R, S, and B.

In general, the larger inhomogeneity effects occurring in base-metal thermocouples mean that the benefit-cost ratio for the calibration of base-metal thermocouples is poor. However, there are a few situations where calibration of base-metal thermocouples can be worthwhile:

- When the temperatures of use are below the temperature where significant thermally induced inhomogeneity effects occur (e.g., below 150 °C or so, depending on the thermocouple type).
- As a sample from a batch made from the same wire, to confirm compliance of the batch with a documentary standard or technical specification.
- As a sample from a batch made from the same wire, as a representative of the batch. Each of the remaining unused thermocouples in the batch may be used once to measure a temperature and then discarded.
- *In situ*, so that the Seebeck coefficient of the wires and the temperature gradient in which the thermocouple is immersed are identical in use and in calibration.
- When the thermocouple has been preconditioned to minimise the thermoelectric changes caused by calibration.

For these situations, the advice provided here is also applicable. Throughout the text, unless otherwise stated, all measurement uncertainties are reported as standard uncertainties.

2. Calibration

The reference functions for thermocouples are defined as exact mathematical equations, and manufacturers usually supply thermocouples conforming to the reference functions within the specified tolerance bands – see Part 1 of this guide for detail [BIPM 2020] and [ASTM 1993]. The deviations of thermocouple output voltage from the reference function, typically less than 1%, vary with different batches of wire, the different wire compositions designed for different environments, and different manufacturers. The aim of calibration is to measure the deviation so corrections can be applied and the uncertainties in measured temperatures reduced.

The calibration must provide:

- the voltage-temperature response of the thermocouple over the temperature range of interest, accompanied by
- the uncertainties in inferred temperatures, and
- the conditions under which the response and uncertainties apply.

The high sensitivity of thermocouples to past temperature exposure means that the procedures for use, the measurement conditions, and the thermoelectric state of the thermocouples should be the same during use and calibration. These requirements ensure that the response and uncertainty determined during calibration correspond to the thermocouple use. For the same reasons, it is essential that critical parts of the calibration procedure, the conditions, and the thermoelectric state of the thermocouple, are reported on the calibration certificate so that they can be reproduced by the user. In general, thermocouple calibrations cannot be applied retrospectively.

2.1. Calibration Methods

Thermocouples may be calibrated in several ways depending on the temperature range, the required accuracy, and the resources of the calibration laboratory, as summarised in Table 1 below. It is recommended [EURAMET 2019] to calibrate from the highest to the lowest temperature, especially if the upper calibration temperature exceeds 1100 °C. Calibrations above 1100 °C potentially cause permanent change to the Seebeck coefficient with the risk of invalidating the calibration at the previously measured lower-temperature points. Exceptions to this recommendation are Type S and Type R and base metal thermocouples when used at temperatures below 1100 °C. Here it can be useful to calibrate at increasing temperatures to prevent reversible thermoelectric changes induced by high-temperature exposure, which can be removed by annealing, from affecting the calibrations at lower temperatures. Also, as discussed in Part I of this guide [BIPM 2020, Sec. 4.8], the selection of annealing and preconditioning procedures appropriate to intended use are important. The different calibration methods are distinguished by the temperature reference used:

ITS-90 fixed points: The melting and freezing points defined by the International Temperature Scale of 1990 (ITS-90) provide the most accurate temperature references and ensure direct traceability to the ITS-90 [Preston Thomas 1990]. Unfortunately, only a small number of fixed points are defined by ITS-90. Also, full-sized ITS-90 fixed points are expensive and take many hours to operate, so calibrations may take several days.

Because the uncertainties achievable with the best thermocouples are relatively large, the requirements for fixed-point realisations are more relaxed than given in the *Guide to the realisation of the ITS-90: Metal Fixed Points for Contact Thermometry* [BIPM 2015]. Often, small fixed-point cells are used to reduce the cost and calibration time at the expense of a negligible increase in uncertainty [BIPM 2018]. The uniformity of the furnace or bath can be poorer, both melting points and freezing points may be used, the fixed-point metal need not be as pure, the mass of metal may be smaller, and thermocouple immersion less.

Miniature fixed points: At temperatures above 1100 °C or so, where furnace and crucible materials are more exotic and expensive, fixed-point calibrations can be made by using miniature cells filled with a few grams of the fixed-point substance [BIPM 2018, Tischler and Koremblit 1982, Edler and Huang 2016]. The concept was first applied with pure metals and later to metal-carbon eutectics [Ongrai *et al*, 2012, Failleau *et al*, 2014, Tucker *et al* 2018]. See [BIPM 2018] for a full summary of the available fixed points for temperatures above 0 °C.

Miniature fixed points also allow the laboratory-based technology of fixed-points to be transferred into industrial settings. Thermocouples assembled with internal fixed points are often described as self-validating. The preferred forms have the same dimensions and connectivity as conventional thermocouples, allowing direct replacement and use under industrial conditions.

Metal-carbon fixed points: Over recent decades, fixed points exploiting metal-carbon eutectics (M-C) and known as high temperature fixed points (HTFPs), have been developed [Yamada *et al* 1999]. Four of the points, Fe-C (~1153 °C), Co-C (1324.26 °C), Ni-C (~1329 °C) and Pd-C (1491.88 °C) may be used for the calibration of noble-metal thermocouples [Edler *et al* 2010, Pearce *et al* 2011, BIPM 2018]. The fixed points are small and achieve uncertainties of 0.1 °C to 0.2 °C.

Wire bridge: A traditional method of calibrating thermocouples, especially noble-metal thermocouples, is to break the junction of the thermocouple and to weld a short section of pure gold (1064.18 °C), palladium (1554.8 °C), or platinum (1768 °C) wire between the two thermoelements. When the thermocouple is heated slowly in a furnace, it typically exhibits a short period when the output voltage is constant, as the wire bridge melts, and then goes open circuit indicating that the wire bridge has melted and broken. The reference temperature is the melting point of the metal bridge.

Typically, about 10 mm of the end of the thermoelements must be sacrificed for each calibration, and the uncertainties tend to be larger than for other methods. Also, care must be taken to avoid tension in the bridge causing premature breakage. In a comparison of wire-bridge gold and palladium calibrations with radiation thermometer calibrations, agreement was within 0.7 K at Au and 1.5 K at Pd, and interpolation between the deviations measured at the Au and Pd points agreed with the radiation thermometer measurements to within 0.2 K to 0.9 K [Crovini *et al* 1987, Edler 1997, Jahan and Ballico 2003b].

Resistance thermometers: For temperatures below 960 °C, standard platinum resistance thermometers (SPRT) may be used [BIPM 2021]. They offer the flexibility of calibrations at many different temperatures, including specific temperatures of interest. For temperatures above 600 °C, care is required to prevent contamination of the SPRTs, so often, calibrations mix SPRTs (below the 550 °C upper limit of salt baths) and use fixed points at higher temperatures. Industrial platinum resistance thermometers (IPRT) may be used but have a reduced temperature range and larger uncertainties.

Reference thermocouples: Most noble-metal thermocouples are calibrated using noble-metal thermocouples previously calibrated using fixed points. The calibrations are carried out in furnaces with the measuring junctions of the thermocouples welded or clamped together. This minimises the effects of temperature gradients in the furnace and ensures the junction temperatures are the same. Welding the junctions together contaminates about 10 mm of wire at the ends of the thermoelements, which must be removed when the thermocouples are rewelded after calibration. The uncertainties are larger than for fixed-point calibrations but satisfactory for most industrial applications. This method also offers the flexibility of calibrations at many different temperatures, including specific temperatures of interest [ASTM 2019, EURAMET 2019].

Radiation Thermometers: Above 960 °C, the ITS-90 is defined using infra-red radiation thermometers [BIPM 2018, Saunders *et al* 2018]. In principle, radiation thermometers should provide the lowest uncertainties for these temperatures, however, radiation thermometers require an unobstructed view of a blackbody cavity, so simultaneous measurements with a thermocouple and a radiation thermometer typically require small-diameter tubular furnaces open at both ends.

Table 1: Typical calibration methods and temperature ranges

Temperature range	Highest accuracy methods	Other methods
Below 250 °C	SPRTs in calibration baths	PRTs in calibration baths
Below 550 °C	ITS-90 fixed points or SPRTs in calibration baths or SPRTs in furnaces	Other noble-metal thermocouples PRTs in calibration baths PRTs in furnaces
Below 1085 °C	ITS-90 fixed points SPRTs, HTSPRTs in furnaces	Other noble-metal thermocouples SPRTs in furnaces Wire bridge
Above 1100 °C	Metal–carbon-eutectic fixed points (HTFPs)	Other noble-metal thermocouples Wire bridge Miniature fixed points IR radiation thermometers

Table 2 gives indicative values for the least uncertainties in the methods of Table 1. The uncertainties given for base metal thermocouples are highly dependent on the operating temperature, thermal pre-treatment of the thermocouples, and the wire and sheath diameters.

Table 2: Indicative values for the least uncertainties for different calibration methods [Crovini *et al* 1987, Ripple and Burns 2005, Burns *et al* 1998, Hill 2002, Sadli *et al* 2005, Webster 2021a, Webster 2021b].

Thermocouple Type	**Temperature Range / °C**	**Fixed points**	**Uncertainty / °C**	
			Fixed-point method	**Comparison method**
S, R	0 - 1100	Sn, Zn, Al, Ag, Cu	0.1 - 0.2	0.2 - 0.3
S, R	>1100	M-C, Pd	0.3	-
B	600 - 1100	Al, Ag, Cu	0.2	0.3
B	>1100	M-C, Pd	0.3	-
Au/Pt	0 - 1000	Sn, Zn, Al, Ag	0.02	-
Pt/Pd	0 - 1100	Sn, Zn, Al, Ag, Cu	0.1	0.2 - 0.3
Pt/Pd	>1100	M-C	0.2	-
T	-200 - 250	-	-	0.5
E	0 -800	Sn, Zn, Al	1.5	1.5
J	0 -760	Sn, Zn, Al	1.5	1.5
K/N	0 - 1100	Sn, Zn, Al, Ag, Cu	1.0	1.0

2.2. *In-situ* Calibrations

In situ calibration is the only method capable of significantly reducing the effects of inhomogeneities. It is often the only method for performing surveys of large furnaces or ovens where documentary standards dictate the use of base-metal thermocouples yet require uncertainties smaller than normally achievable. This requirement commonly occurs with spatial surveys of heat-treatment furnaces used in the aviation industry.

The essence of the method is to leave the thermocouple fixed firmly in its normal installation and bring the reference thermometer to the thermocouple rather than the other way around. This ensures that the temperature gradients and the Seebeck coefficients along the length of the thermocouple are the same in use as during calibration. Therefore, the errors due to inhomogeneity are the same in use as in calibration.

Figure 1 gives an overview of the calibration and shows how the method is applied to the spatial survey of a large furnace. In the calibration phase, all the survey thermocouples are pulled through an aperture in the furnace wall and tied together with the reference thermometer, typically a noble metal thermocouple or platinum resistance thermometer. It may be helpful to additionally wrap insulation around the bundle to reduce temperature gradients and help ensure they are all at the same temperature. The survey thermocouples are then clamped at the wall of the furnace so that the sections of thermocouples passing through the furnace wall cannot move. The sections of wire passing through the wall are exposed to almost all the temperature gradient and therefore generate almost all the voltage. Clamping the wires in place there ensures that the voltage generated is the same in use as in calibration. Note that enough of the length of each survey thermocouple must be pulled into the furnace so that they can be easily placed in their respective survey positions without being unclamped.

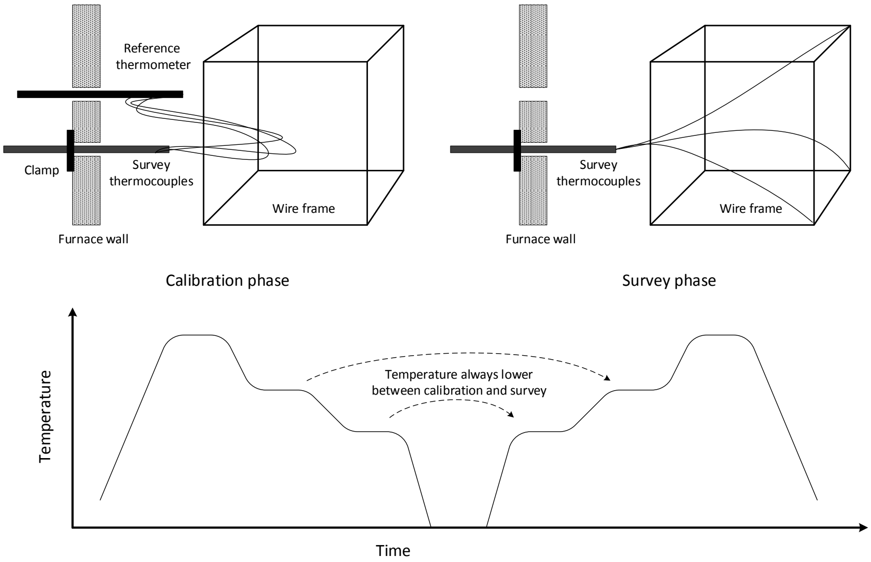

Figure 1: *In situ* calibration of thermocouples in a furnace or oven survey.

The furnace is then set to the required temperature for a couple of hours to allow the thermocouples to stabilise, and comparison is made with the reference thermometer. If the furnace is to be surveyed at more than one temperature, the calibration should start at the highest temperature and work downwards.

Once the thermocouples have been calibrated, the furnace is cooled down, and the thermocouples are redistributed to the survey locations while ensuring the clamping is unchanged. Depending on whether the survey is carried out with or without a load, it may be helpful to use a wire frame to hold the thermocouples in place. The survey is then carried out proceeding from the lowest temperature to the highest temperatures. The sequence is important: once calibrated at a given temperature, a survey thermocouple is not exposed to a higher temperature before it is used in the survey.

2.3. Calibration Equations

Thermocouple calibration equations correct for the deviation, $\Delta V(t)$, between the thermocouple output, $V(t)$, and its reference function, $V_{\mathrm{ref}}(t)$,

$$\Delta V(t) = V_{\mathrm{ref}}(t) - V(t)\,. \tag{1}$$

The reference function models the main features in $V(t)$ ensuring that the deviation is smooth and small, usually less than 1% of the measured signal. The correction equation developed from the calibration measurements (often called the deviation function) is usually a simple polynomial that closely approximates the deviation,

$$\Delta V(t) \cong a + bt + ct^2 + dt^3 + \dots\,. \tag{2}$$

The practical effect of using the deviation for calibration is that only a few calibration points are required to characterise the thermocouple response.

Typically, two or three terms in Equation (2) are sufficient for noble metal thermocouples while as many as six terms may be required for base metal thermocouples used over a wide temperature range. Cubic polynomials are commonly used as they accommodate offset errors (the a term of (2)), linear scale errors (the b term), symmetric non-linearity (the c term), and antisymmetric non-linearity (the d term). For noble-metal thermocouples calibrated over ranges including 0 °C, where the thermocouple output is nominally zero, the first coefficient, a, is usually set to zero (see Example 5.1 below).

The number of calibration points used usually depends on availability of reference temperatures (which depends on the method chosen) and the required temperature range. Because there are relatively few fixed points and they occur at widely spaced temperature intervals, there may be few points available. If the calibration employs a reference thermometer, such as another thermocouple, platinum resistance thermometer, or radiation thermometer, the number of calibration points can be very much larger and spaced more closely. There must be at least as many calibration points as free parameters in the calibration equation.

When the number of calibration points is equal to the number of coefficients in the calibration equation, the equation passes through each of the points as shown in Figure 2(a) and is said to interpolate between the calibration points. Conventionally, the coefficients are determined by solving simultaneous equations, but in Sec. 3 we show how the calibration equation can be written directly in terms of the measurements.

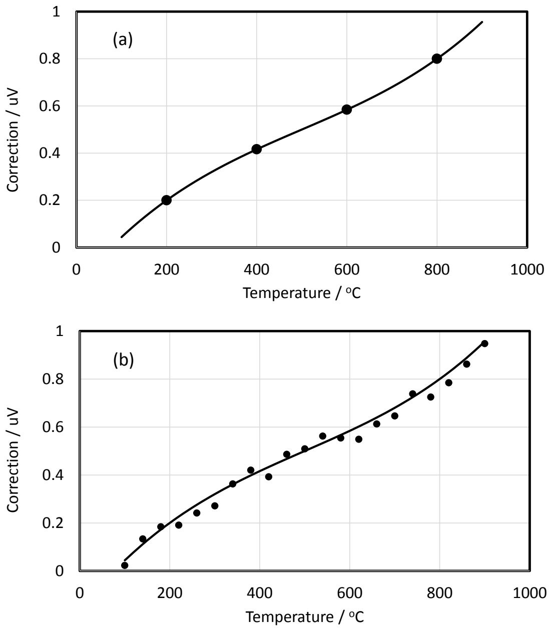

Figure 2: A cubic correction equation determined by (a) interpolation through a minimum of calibration points, and (b) least-squares fit of the equation to surplus of calibration points.

If the number of calibration points exceeds the number of coefficients in the equation, a least-squares fit is used to determine the coefficients (Figure 2(b)). The least-squares fit finds the equation that passes closest to the measured points by minimising the sum of the squares of the differences between the points and the equation. Most spreadsheet applications have several options for performing least-squares fits (a.k.a. linear regression), and well-proven software is available from the NAG software library [https://www.nag.com/content/nag-library] and is often included in commercial graphing applications. For an explanation of the least-squares method, see [Bevington and Robinson 2003, Press *et al* 2007].

2.4. Reporting

The documentary standard, ISO 17025 [ISO/IEC 2017], which defines competence for test and calibration laboratories, requires laboratories to include the following information on calibration certificates:

- the title “Calibration Certificate”
- the name, address, and location of the calibrating laboratory,
- the location of the calibration site if different from the laboratory,
- the name, address, and location of the client,
- the means to uniquely identify the certificate, usually a number traceable to measurement records,
- the means to uniquely identify the calibrated equipment, usually a brief description, the manufacturer, model, and serial numbers of all items,
- the date(s) when the calibration(s) were carried out,
- the date when the report is completed,
- identification or description of the calibration method, particularly where there are departures from standard methods,

- the results and observations and/or conclusions derived from the measurements,
- conditions under which the calibration was carried out,
- a statement of traceability to the appropriate national standards and to the appropriate temperature scale (ITS-90 or the thermodynamic scale),
- a statement of the uncertainties in reported results,
- the author(s) of the report and/or personnel responsible for the tests,
- the conditions under which the report may be reproduced,
- an endorsement by an independent accrediting body,
- on each page, the page number and the total number of pages.

For thermocouple calibrations, the annealing procedure, the measurement conditions, and uncertainty are especially important. There are three main concerns:

Preferred Thermoelectric State: To achieve the lowest practical uncertainties, the thermocouple must be restored to the same convenient and reproducible thermoelectric state prior to calibration and prior to use. For platinum-rhodium thermocouples used below 800 °C, the most stable and reproducible state requires the thermocouple to be annealed at 1100 °C until stable, followed by a minimum of a 2 hr vacancy anneal at 450 °C. If used above 800 °C, the best thermoelectric state requires the anneal at 1100 °C to be followed by quenching in air to room temperature. The difference between measurements in the two thermoelectric states can be several tenths of a degree [BIPM 2020 Section 4.8, Webster 2015, McLaren and Murdock 1979, Bentley 1998a, Jahan and Ballico 2010]. Therefore, it is essential that the calibration certificate describes the process for placing the thermocouple in its preferred state. For example, the certificate might report “The thermocouple was annealed at 1100 °C until stable, then at 450 °C for 2 hrs, prior to calibration”.

To achieve the best estimates of uncertainty, thermocouples must be scanned for homogeneity, ideally, before calibration (the as-received state), after the anneal and prior to calibration (the preferred state for use), then after calibration and final anneal, as confirmation of stability. This procedure yields the most realistic estimate of uncertainties due to inhomogeneity and provides information on stability.

Measurement Conditions: As shown in Section 3 (below), there may be several opportunities to minimise or eliminate some measurement errors through careful experimental design. In effect, the thermocouple is calibrated under conditions that are replicated in use so that some errors cancel. Those conditions should be described on the certificate. Conditions covered may include the type and use of the reference junction, immersion conditions, and the DVM used to make the voltage measurements.

Definition of total uncertainty: There are two conventions for the reporting of total uncertainty of a calibration. One convention is to report the uncertainty in the correction equation. This means that the user must add additional uncertainties arising during use, which includes the effects of inhomogeneities – usually the dominant source of uncertainty. Necessarily, this option assumes that the user has the facilities and competence to assess the additional uncertainties.

The second and preferred option is to report the uncertainty in temperatures inferred using the correction equation, that is, with the additional uncertainties due to use that the user may be unable to assess (see Example 5.1 for an example). Necessarily, this forces the calibration laboratory to make measurements of inhomogeneity. Note that ISO 17205, the documentary standard covering accreditation of calibration laboratories, forbids the inclusion of uncertainties related to the drift of instruments after calibration. Because drift is highly dependent on operating conditions and usage, it is the users' responsibility to assess and manage these contributions to uncertainty. Typically, the user makes the assessment using the observed drift between successive calibrations.

Whichever uncertainty option is chosen, the calibration certificate should clearly state the meaning of the reported uncertainty.

3. Measurement Model and Uncertainty Budget

This section derives the measurement model and uncertainty budget for the use of a thermocouple. The derivation is provided in detail (i) for completeness (ii) to determine the correct form of sensitivity coefficients, and (iii) to highlight aspects of measurement design enabling error cancelation. In most uncertainty analyses, some of the terms identified in the budget may be able to be neglected, as the examples in Section 5 show.

3.1. Measurement Model

The measurement model is the equation relating the thermocouple voltage to all other physical variables that may affect the measurement. We start with the basic equation for the thermocouple voltage from Part 1 of this guide [BIPM 2020],

$$V = V(t_\mathrm{m}) - V(t_\mathrm{r}) , \tag{3}$$

where t_m and t_r are the temperatures of the measurement and reference junctions. In practice, there are small errors causing the measured junction temperatures to differ from the true junction temperatures, there are errors in the dc voltages recorded by the digital voltmeter (DVM), and there may errors in the reference-junction compensating voltage, V_cj, (if used), so that the recorded thermocouple voltage is

$$V_\mathrm{meas} = V(t_\mathrm{m} - \Delta t_\mathrm{m}) - V(t_\mathrm{r} - \Delta t_\mathrm{r}) - \Delta V_\mathrm{dvm}(t_\mathrm{m}) + V_\mathrm{cj}(t_\mathrm{r}) , \tag{4}$$

where the delta operator, Δ, indicates 'a small error in' the adjacent quantity. During calibration, the thermocouple voltage is measured at several temperatures and the values of the deviation at each calibration temperature, t_i, are calculated from the measured voltages and the reference function,

$$\Delta V_i = V_\mathrm{ref}(t_i) - V_{\mathrm{meas},i} \tag{5}$$

and used to determine the coefficients in the correction, Equation (2). Then, during use of the calibrated thermocouple, the temperature is inferred from the measured voltage by using the calibration equation and the reference function to convert between voltage and temperature:

$$V_{\mathrm{ref}}(t_{\mathrm{m}}) = V_{\mathrm{meas}} + \Delta V(t_{\mathrm{m}}), \tag{6}$$

where t_{m} is the measured temperature. By combining Equations (4), (5) and (6), expanding the terms in the thermocouple response, $V(t)$, as a first-order Taylor series, and rearranging the equation in terms of the error in the measured temperature, we get

$$\begin{aligned}\Delta t_{\mathrm{meas}} = \frac{1}{S(t_{\mathrm{m}})} \big[& V_{\mathrm{ref}}(t_{\mathrm{m}}) - V(t_{\mathrm{m}}) - \Delta V(t_{\mathrm{m}}) \\ & + S(t_{\mathrm{m}})\Delta t_{\mathrm{m}} \\ & + S(t_{\mathrm{r}})\Delta t_{\mathrm{r}} \\ & + V(t_{\mathrm{r}}) - V_{\mathrm{cj}}(t_{\mathrm{r}}) \\ & - \Delta V_{\mathrm{dvm}}(t_{\mathrm{m}}) \big]\end{aligned} \tag{7}$$

where $S(t) = dV(t)/dt$ is the Seebeck coefficient at temperature t. Equation (7) is written in five rows to identify the five distinct groups of errors for the uncertainty budget:

- Row 1: error due to the difference between the true thermocouple deviation and the deviation measured during the calibration,
- Row 2: error in the measurement junction temperature,
- Row 3: error in the reference junction temperature,
- Row 4: error in the reference junction compensation voltage (if used), and
- Row 5: error in the measured voltage due to errors in the digital voltmeter.

Each error identified here may have several causes, as explained in Section 4 below.

Equation (7) implicitly includes the calibration measurements within the calibration equation, ΔV™, in the first row. For the uncertainty analysis, we must expand this term so we can directly evaluate the effect of errors in the calibration measurements. For the purposes of illustrating the analysis, consider the case of a four-point calibration with a full cubic calibration equation. The case of an equation fitted by least-squares is similar and will be discussed shortly.

We would normally find the calibration equation, (2), by substituting the measured values for the four deviations, ΔV_i, and using the method of simultaneous equations to determine the coefficients a, b, c, and d. However, the uncertainty analysis is simpler if the calibration equation is written in an alternative form where the measured deviations appear as coefficients in the equation [White and Saunders 2007]:

$$\Delta V(t) = \Delta V_1 F_1(t) + \Delta V_2 F_2(t) + \Delta V_3 F_3(t) + \Delta V_4 F_4(t) = \sum_{i=1}^{4} \Delta V_i F_i(t) \,. \tag{8}$$

The $F_i(t)$ are a family of interpolating functions (called Lagrange polynomials). The first interpolating function is,

$$F_1(t) = \frac{(t-t_2)(t-t_3)(t-t_4)}{(t_1-t_2)(t_1-t_3)(t_1-t_4)} \,. \tag{9}$$

The function takes the value of 1.0 exactly at $t = t_1$ and is zero at all other calibration temperatures (where $t = t_2$, t_3, or t_4). Therefore, if we multiply $F_1(t)$ by ΔV_1, (as in Equation (8)), we can be sure $\Delta V_1 F_1(t)$ passes through the first calibration point, $(t_1, \Delta V_1)$, yet is zero at the other calibration points. The other interpolating functions, $F_2(t)$, $F_3(t)$, $F_4(t)$, have the same form as (9):

$$\begin{aligned} F_2(t) &= \frac{(t-t_1)(t-t_3)(t-t_4)}{(t_2-t_1)(t_2-t_3)(t_2-t_4)}, \\ F_3(t) &= \frac{(t-t_1)(t-t_2)(t-t_4)}{(t_3-t_1)(t_3-t_2)(t_3-t_4)}, \\ F_4(t) &= \frac{(t-t_1)(t-t_2)(t-t_3)}{(t_4-t_1)(t_4-t_2)(t_4-t_3)}, \end{aligned} \tag{10}$$

so that they also take the value 1.0 exactly at the calibration temperature for which they are named (2, 3, or 4) and zero exactly at the other calibration points. Note that the functions all have the same mathematical form, but have the subscripts exchanged. Once the form of the functions is recognised, it is relatively easy to write down the interpolating functions for polynomials of any order.

Since each product, $\Delta V_i F_i(t)$, passes through its corresponding calibration point and is zero at the others, we can be sure that the sum, Equation (8), passes through all the calibration points. Since each interpolating function is a cubic polynomial, the sum is also a cubic polynomial, and therefore Equation (8) is the unique cubic polynomial that passes through all four calibration points; it is identical to Equation (2) but written in a different form.

Writing the correction equation in this longer form may seem an unnecessary complication, but it means that we can develop the propagation of error and uncertainty equations directly in terms of the measurements. If we differentiate Equation (8) with respect to ΔV_1, we get $F_1(t)$. That is, $F_1(t)$ is the sensitivity coefficient for errors in the measured deviation, ΔV_1. $F_1(t)$ tells us how errors in measurements of ΔV_1 affect measurements at other temperatures. The sensitivity coefficient for errors in the temperature t_1 is slightly more complicated because it also depends on the slope of the calibration equation at the calibration temperature:

$$\frac{d\Delta V(t)}{dt_1} = -\left.\frac{d\Delta V(t)}{dt}\right|_{t=t1} F_1(t)\,. \tag{11}$$

By differentiating Equation (8) with respect to each of the nine measurements (four calibration points, each with a measurement of voltage and temperature, and the voltage measurement at the unknown temperature), we get the propagation-of-error equation:

$$d\Delta V(t) = \sum_{i=1}^{4} F_i(t)\, d\Delta V_i - \sum_{i=1}^{4} \left.\frac{d\Delta V(t)}{dt}\right|_{t=ti} F_i(t)\, d\Delta t_i + \frac{d\Delta V(t)}{dt}dt\,. \tag{12}$$

Equation (12) collects three groups of error terms: errors associated with the voltages measured during calibration (under the first summation), the errors associated with the reference temperatures measured during calibration (under the second summation), and errors in the voltage measured at the unknown temperature (the last term).

Now we can combine Equations (12) and (7) and collect all like terms, to get the full propagation-of-error equation for a temperature measurement using a calibrated thermocouple:

$$\begin{aligned}\Delta t_{\mathrm{meas}} = \frac{1}{S(t_{\mathrm{m}})}\Big\{ & V_{\mathrm{ref}}(t_{\mathrm{m}}) - V(t_{\mathrm{m}}) + \sum_i F_i(t_{\mathrm{m}})\Delta V_i(t_{\mathrm{i}}) \\ & + S(t_{\mathrm{m}})\Delta t_{\mathrm{m}} - \sum_i S(t_{\mathrm{i}})F_i(t_{\mathrm{m}})\Delta t_i \\ & + S(t_{\mathrm{r}})\Delta t_{\mathrm{r}} - S(t_{\mathrm{r}})\sum_i F_i(t_{\mathrm{r}})\Delta t_{\mathrm{r},i} \\ & + V(t_{\mathrm{r}}) - V_{\mathrm{cj}}(t_{\mathrm{r}}) - \sum_i F_i(t_{\mathrm{m}})\left[V_i(t_{\mathrm{r}}) - V_{\mathrm{cj},i}(t_{\mathrm{r}})\right] \\ & + \Delta V_{\mathrm{dvm}}(t_{\mathrm{m}}) - \sum_i F_i(t_{\mathrm{m}})\Delta V_{\mathrm{dvm},i}(t_{\mathrm{i}})\Big\}. \end{aligned} \tag{13}$$

This equation identifies all the sensitivity coefficients required for the uncertainty budget.

Before we proceed to the discussion of individual terms in Equation (13), it will be helpful to highlight some important properties of the interpolating functions. The interpolating functions, $F_{\mathrm{i}}(t)$ can be thought of as a mathematical device for converting samples of a function into a continuous function. For example, if we have four samples of a function $g(t)$ at specific temperatures, namely $g(t_1)$, $g(t_2)$, $g(t_3)$, and $g(t_4)$, we can reconstruct the continuous function $g(t)$ simply by multiplying each sample by its corresponding interpolating function and summing the results:

$$g(t) = \sum_i g(t_i)F_i(t)\ . \tag{14}$$

The calibration Equation, (8), is constructed in this way. But there is a limitation; if the interpolating functions are cubic, as here, then the most complicated function that can be accurately reconstructed is a cubic polynomial. If the function is more complicated than cubic, the calibration equation is an approximation. The residual errors caused by an overly simple calibration equation are called interpolation errors (Sec.4.1.1).

Because the interpolation functions interpolate all cubic functions exactly, we can use Equation (14) to generate a set of identities:

$$\sum_{i=1}^{4} t_i^n F_i(t) = t^n, \quad n = 0..3\ . \tag{15}$$

which will be useful for simplifying uncertainty expressions.

It also follows from Equation (14), that collections of terms with a form:

$$g(t) - \sum_i g(t_i) F_i(t) , \tag{16}$$

will cancel and be close to zero. In Equation (13) there are five collections of terms where cancelation can occur:

- Row 1: terms relating to the calibration equation and thermocouple deviation.
- Row 2: terms relating to errors in the measurement junction temperature.
- Row 3: terms relating to errors in the reference junction temperature.
- Row 4: terms relating to the reference junction compensation voltage.
- Row 5: terms relating to the voltage measurement by the digital voltmeter.

The main purpose of the calibration is to measure and correct the deviation through the cancellation represented in Row 1 of Equation (13). However, with careful design of the measurement and calibration we can use the other cancellation effects to minimise the uncertainty. These possibilities are discussed in Section 4.

Figure 3 shows the four interpolating functions, $F_1(t)$, $F_2(t)$, $F_3(t)$, and $F_4(t)$ for calibration temperatures of 0 °C, 231.928 °C, 419.527 °C, 660.323 °C (the ice, tin, zinc, and aluminium points). Note the locations of the ones and zeros of the functions and the cubic (S shape) behaviour of each.

The bold curve of Figure 3 shows the root-sum-square (RSS) of the four functions, $\left[\sum F_i^2(t)\right]^{1/2}$. This curve gives an indication of how the total uncertainty varies with the measured temperature. For temperatures between the calibration points, (i.e., $t_1 \le t \le t_4$), the RSS is close to 1.0, and there are cases where this approximation can be used.

Extrapolation is the process of extending the calibration equation beyond the range of the calibration. The SUM curve in Figure 3 also shows that the total uncertainty increases rapidly (in proportion to t^3 for a cubic equation) outside the calibration points. For almost all calibration equations, extrapolation amplifies the effects of uncertainties [Giorgio 2013, Bentley 1998b, White and Saunders 2007]. Generally, calibration points should be chosen to span the intended range of use to avoid extrapolation and uncertainty amplification.

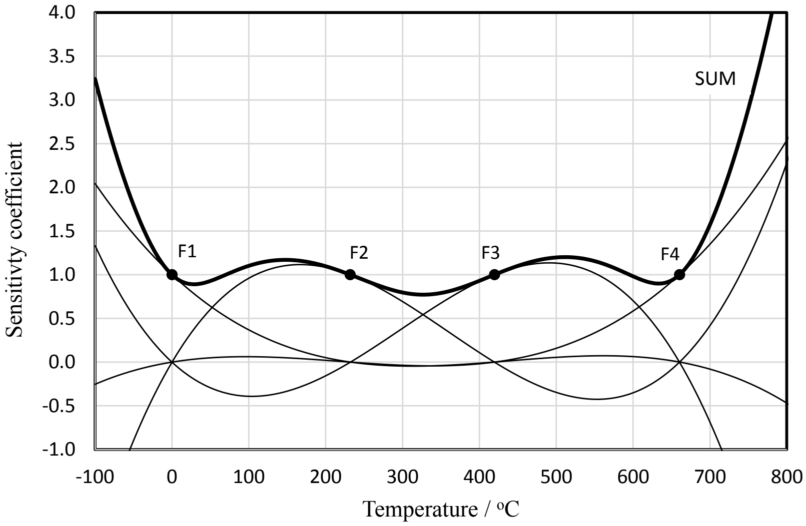

Figure 3: The four interpolating functions for a calibration at the ice, tin, zinc, and aluminium fixed points. SUM (bold) is the root-sum-square of the four functions.

For least-squares fitted equations, the propagation-of-error equation has the same form as Equation (13) except that the number of terms in the summations is equal to the number of measurements, and the interpolating functions are no longer Lagrange polynomials. Nevertheless, the general observations about the nature of the calibration equation and interpolation apply. The main difference between equations determined by least-squares fits and interpolation is that the uncertainties due to random errors are reduced with least-squares fits. If there are N calibration points, and ρ free parameters in the deviation function, and the uncertainties are entirely due to random errors, the total uncertainty curve has the same shape as the SUM curve of Figure 3, but the values are lower by a factor of about $\sqrt{\rho / N}$ [White and Saunders 2007, White 2016]. For further details on uncertainty propagation with calibration equations see [White and Saunders 2007, White 2016, Tellinghuisen 2020] and standard texts on least squares [Bevington and Robinson 2003; Press *et al* 2007, Eberly 1999].

3.2. Uncertainty Budget

Uncertainty budgets should list all uncertainty contributions with each labelled according to physical cause or origin. Labelling the terms according to origin or cause helps avoid double counting of contributions, which often occurs when generic terms like repeatability or reproducibility are used. Table 3 presents an outline of an uncertainty budget, based on Equation (13), with the five groups of error expanded to identify the possible physical origins of the various contributions. The table separates sources of uncertainty associated with the use of the thermocouple on the left-hand side of the table, while the terms associated with the calibration of the thermocouple are on the right-hand side of the table. Detailed discussion of each source of uncertainty and methods of assessment are presented in Section 4.

Table 3: Outline of the uncertainty budget with the sources of uncertainty, sensitivity coefficients, and comments on the assessment of the effects.

Source of Uncertainty	**Uncertainty in use**	**Uncertainty in calibration**
Thermoelectric deviations	$\frac{V_{\mathrm{ref}}(t_{\mathrm{m}})-V(t_{\mathrm{m}})}{S(t_{\mathrm{m}})}$	$\frac{\sum F_i(t_{\mathrm{m}})\Delta V_i(t_{\mathrm{i}})}{S(t_{\mathrm{m}})}$
Inhomogeneity	Use homogeneity scan, Type B assessment otherwise.	Use homogeneity scan, Type B assessment otherwise.
Interpolation error	Assumed to be negligible.	Assumed to be zero.
Insulation breakdown	Non-zero only for long MIMS or very high-temperature TCs	Non-zero only for long MIMS or very high-temperature TCs
Drift in TE state	User must evaluate.	Zero (excluded by ISO17025)
Measurement Junction Temperatures	Δt_{m}	$\frac{\sum S(t_{\mathrm{i}})F_i(t_{\mathrm{m}})\Delta t_i}{S(t_{\mathrm{m}})}$
Thermal effects	Immersion, gradients, heating effects temperature fluctuations,	Immersion, gradients, heating effects temperature fluctuations,
Reference Temperature	Zero, not applicable	Reported on certificate for reference thermometers or CMCs
Reference Junction Temperatures	$\frac{S(t_{\mathrm{r}})\Delta t_{\mathrm{r}}}{S(t_{\mathrm{m}})}$	$\frac{S(t_{\mathrm{r}})\sum F_i(t_{\mathrm{r}})\Delta t_{\mathrm{r},i}}{S(t_{\mathrm{m}})}$
Thermal effects	Immersion, gradients, heating effects temperature fluctuations,	Immersion, gradients, heating effects temperature fluctuations,
Reference junction compensation voltage	$\frac{V(t_{\mathrm{r}})-V_{\mathrm{cj}}(t_{\mathrm{r}})}{S(t_{\mathrm{m}})}$	$\frac{\sum F_i(t_{\mathrm{m}})\left[V_i(t_{\mathrm{r}})-V_{\mathrm{cj},i}(t_{\mathrm{r}})\right]}{S(t_{\mathrm{m}})}$
Junction temperature	Thermometer uncertainty.	Thermometer uncertainty.
Thermal effects	Immersion, gradients, heating effects temperature fluctuations,	Immersion, gradients, heating effects temperature fluctuations,
Voltage generation	Uncertainty in compensation leads, error in voltage generator	Uncertainty in compensation leads, error in voltage generator
Voltage measurement	$\frac{\Delta V_{\mathrm{dvm}}(t_{\mathrm{m}})}{S(t_{\mathrm{m}})}$	$\frac{\sum F_i(t_{\mathrm{m}})\Delta V_{\mathrm{dvm},i}(t_{\mathrm{i}})}{S(t_{\mathrm{m}})}$
DVM	As reported on Calibration certificate for DVM	As reported on Calibration certificate for DVM
Electromagnetic interference	Normally negligible	Normally negligible

4. Sources of Uncertainty

Part 1 of this guide [BIPM 2020] provided detailed explanations of the physical origins of effects leading to errors in thermocouple measurements. This section discusses the assessment of the contributions of those errors to measurement uncertainty.

4.1. Thermoelectric Deviations and Inhomogeneity

Manufacturers usually supply thermocouples conforming to the reference functions within the specified tolerance bands. During calibration, the deviation between the actual response of the thermocouple and reference function is measured so corrections can be applied. Any effect causing the measured deviation to differ from the actual deviation of the thermocouple will cause errors and uncertainty in use.

4.1.1. Interpolation Error

Almost always, calibration equations approximate the complicated behaviour of measuring instruments. The difference between the true behaviour and the calibration equation is called interpolation error. Figure 4 illustrates the main characteristics of interpolation error by plotting the error for a non-linear temperature sensor using two different calibration equations. The first equation approximates the sensor response with a straight line determined from two calibration points (0 °C and 100 °C), while the second is a quadratic calibration equation with three calibration points (0 °C, 50 °C, and 100 °C). As the plots show, more complex equations tend to yield better approximations. But more complex equations also require more calibration points and are less convenient to use, and in general we must find a compromise. For example, although there is some residual interpolation error with the quadratic equation (the blue curve), it may be perfectly adequate if we only require the thermometer to have an uncertainty below 0.1 °C.

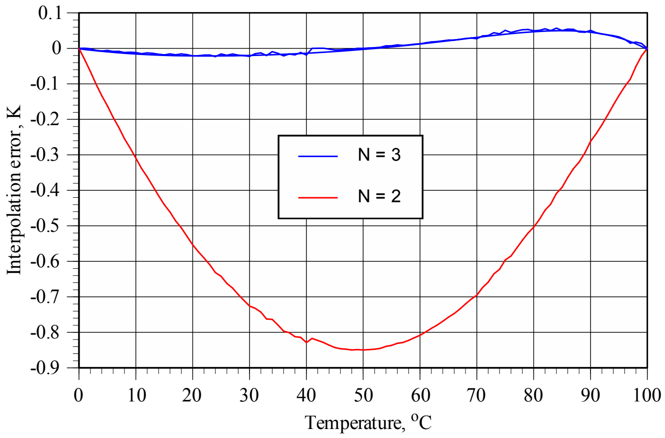

Figure 4: Interpolation error for a temperature sensor using a linear ($N = 2$) and quadratic ($N = 3$) calibration equations.

Also, as shown in Figure 4, the interpolation error is zero at the calibration points. Therefore, interpolation error can be rendered negligible by (i) choosing an appropriate mathematical function for the calibration equation, or (ii) by choosing calibration points to match critical measured temperatures in use.

Where a calibration equation is fitted using least squares (Figure 2b), the zeros in the interpolation error no longer occur at the calibration points but are approximately evenly spaced over the calibration range. Least-squares fits have the advantage of enabling a direct comparison of the suitability of calibration equations by comparing the expected uncertainty with the standard deviation of the residual errors of the fits:

$$u_{\mathrm{fit}} = \sqrt{\frac{\sum \left(\Delta V_i - \Delta V(t_i) \right)^2}{N - \rho}} \, . \tag{17}$$

where ΔV_i are the measured deviations at the temperatures t_i, $\Delta V(t_i)$ are the values of the fitted calibration equation evaluated at t_i (i.e., the residuals are the differences between the lines and the points in Figure 2b), and ρ is the number of fitted coefficients in the equation. Generally, u_{fit} decreases as the number of terms in the calibration equation increases (e.g., progressing from linear, to quadratic, then cubic polynomials). Once the calibration equation is sufficiently complicated to ensure the interpolation error is negligible, u_{fit} will cease to improve significantly and further increases in the complexity of the equation have little benefit. If the form of the calibration equation is appropriate, the uncertainty due to interpolation error should be negligible compared to other uncertainty contributions.

There have been a few studies of interpolation error in thermocouple calibrations. Burns *et al.* [Burns, 1998], assigned uncertainties to the Pt/Pd reference function by determining the effect of the uncertainty in each data point used in its derivation. The scatter of the data was used to estimate uncertainties of the Type S, R and Au/Pt reference functions using Working-Hotelling confidence bands [Burns *et al* 1992a, Burns *et al* 1992b, Burns *et al* 1992c]: these are likely to be underestimates of the actual uncertainties of the reference functions because the data obtained within a single piece of apparatus are highly correlated.

Burns *et al* [Burns, 1998] also compared a Type S thermocouple that was very close to the Type S reference function to one of the Pt/Pd thermocouples used to derive the Pt/Pd reference function: the deviations between Type S and Pt/Pd were smooth from 720 °C to 1500 °C and within expectations, leading to the conclusion that the Type S reference function models Type S behaviour well.

Bentley [Bentley, 1998b] analysed the calibration data of 367 Type R and S thermocouples and estimated the fit uncertainty (k = 2) to be 0.1 µV + $10^{-4} \cdot V$) for calibration at 0, 30, 157, 232, 321, 420, 660, 962 and 1064 °C, and (1 µV + $2.5 \cdot 10^{-4} \cdot V$) for calibration at 0, 321, 660, 962 and 1064 °C.

Ripple and Burns [Ripple and Burns, 2005] fitted quadratic deviation functions to the calibration data of 21 Au/Pt thermocouples and the systematic discrepancy between data obtained by fixed-point measurements and data obtained by comparison with an SPRT at nearby temperatures was used as an estimate of the fitting uncertainty: this uncertainty was 0.04 µV at 1000 °C, 0.026 µV from 962 °C to 157 °C and decreased to 0.014 µV near 10 °C. For Types R and S, Au/Pt and Pt/Pd, the deviations are usually small and the curve only slightly non-linear; a polynomial of second to fourth degree should fit the data adequately.

Burns and Gallagher [Burns and Gallagher, 1966] plotted deviations of several thermocouples from the Type B reference function: it appears that a low order polynomial should fit the data to within a microvolt or two at temperatures below 1100 °C, but above 1100 °C the data used to determine the reference function have significantly more scatter, and the uncertainty of the reference function may be as high as 2 µV at 1700 °C.

Type B thermocouples are roughly twice as susceptible to oxidation effects and ordering effects as are Types R or S, resulting in larger non-linearities in the deviation polynomial of a Type B in the range 600 °C to 900 °C and in the range between 250 °C and 550 °C [Webster and Edler, 2017].

4.1.2. Inhomogeneity

Inhomogeneities are variations in the Seebeck coefficient along the length of the thermocouple wires. Inhomogeneity is almost always the largest source of uncertainty in thermocouple measurements.

Inhomogeneity can be measured by progressively passing the thermocouple through a narrow temperature gradient and monitoring changes in the voltage. Figure 5 illustrates the principle [Webster and White 2015]. An ideal homogeneity scanner has two isothermal zones at different temperatures separated by a few millimetres. The thermocouple under test is immersed through the cold zone to the hot zone, so that a steep temperature gradient is imposed on the thermocouple in the vicinity of the gap. This is the only part of the thermocouple producing any voltage. By slowly immersing the thermocouple through the gradient, the Seebeck coefficient at different locations on the thermocouple can be measured and compared.

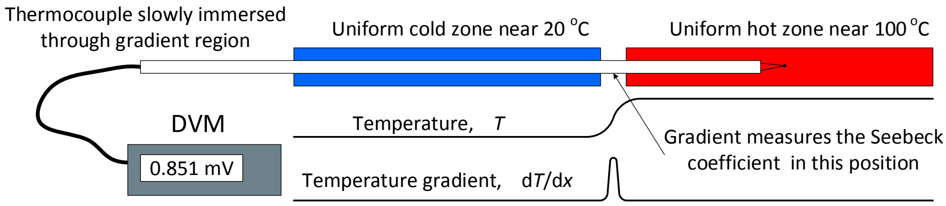

Figure 5: Measurement principle for a homogeneity scanner showing a schematic of the scanner, the temperature profile through the scanner, and the temperature gradient.

Homogeneity scanners with the highest spatial resolution use heat-pipes for the two isothermal zones yielding a spatial resolution of a few millimetres [Webster *et al* 2015]. The temperature of the hot zone should be below 150 °C or so, to ensure that the act of scanning the thermocouple does not induce changes in the Seebeck coefficient [Webster 2014]. For thermocouples with low output at low temperatures (e.g., Type B), it may be necessary to scan at higher temperatures [Webster *et al* 2015, Webster *et al* 2016, Kim *et al* 2017]. The cold zone of the scanner and reference junction should be at ambient temperature to ensure the thermocouple is not exposed to any other gradients. The temperatures of the hot and cold zones must be accurately measured.

Useful scans can also be obtained by slowly immersing the thermocouple into a calibration bath or a small diameter tube furnace [Hill and Gee 2013, Tamba 2011, Reed (Parts I and II) 1992, Bentley and Meszaros 1989, Bentley 2000]. A fan or air blower generating a constant-temperature air flow can be used to cool the thermocouple just outside the bath or furnace to narrow the temperature gradient and improve the spatial resolution of the scan.

The scanner measures the average Seebeck coefficient over the range of temperatures between the hot and cold zones, and over the narrow length of the thermocouple where the gradient occurs (determined by the small peak in the lower curve in Figure 5). The measured average Seebeck coefficient is:

$$\bar{S}(x) = \frac{V(x)}{t_\mathrm{h} - t_\mathrm{c}} \;, \tag{18}$$

where $V(x)$ is the voltage measured when the part of the thermocouple at position x along the thermocouple length is located at the peak of the scanner gradient, t_h is the temperature of the hot zone, and t_c is the temperature of the cold zone. The measured Seebeck coefficient can be compared to that expected from the reference function for the same temperature interval,

$$\overline{S_\mathrm{ref}}(x) = \frac{V_\mathrm{ref}(t_\mathrm{h}) - V_\mathrm{ref}(t_\mathrm{c})}{t_\mathrm{h} - t_\mathrm{c}} \;. \tag{19}$$

Hence, the measured error in the Seebeck coefficient is:

$$\overline{\Delta S}(x) = \bar{S}(x) - \overline{S_\mathrm{ref}}(x) \;. \tag{20}$$

Figure 6 plots the error in the Seebeck coefficient for a high-quality Type S thermocouple and illustrates how the coefficient varies with the position along a thermocouple. In this case, the mean Seebeck coefficient error over the usable length of the thermocouple is –0.008 µV/°C, and the standard deviation is 0.0008 µV/°C. The mean Seebeck coefficient error equivalent to about –0.8 °C, would be corrected by the calibration equation. The uncertainty of 0.0008 µV/°C due to thermoelectric inhomogeneity is assumed to be normally distributed and is equivalent to about 0.08 °C for temperatures near 1000 °C.

The scan shown in Figure 6 is typical of the highest quality Type S thermocouples [Jahan and Ballico 2007]. The root mean square (RMS) inhomogeneity is typically lower than ± 0.02 % in new Pt-Rh thermocouples [Bentley 1998a] and ± 0.2 % in new base-metal thermocouples [Webster 2014, Webster and White 2015, Webster 2021c].

Because inhomogeneity is usually the dominant source of uncertainty in thermocouple measurements, it is essential to perform scans if reliable estimates of uncertainty are required. In addition to the uncertainty assessment, homogeneity scans provide confidence in the proper functioning of a thermocouple. Scans should be smooth and not exhibit large highly localised inhomogeneities, which are often the signature of serious damage (see Sec. 5.2, Part 1 [BIPM 2020]).

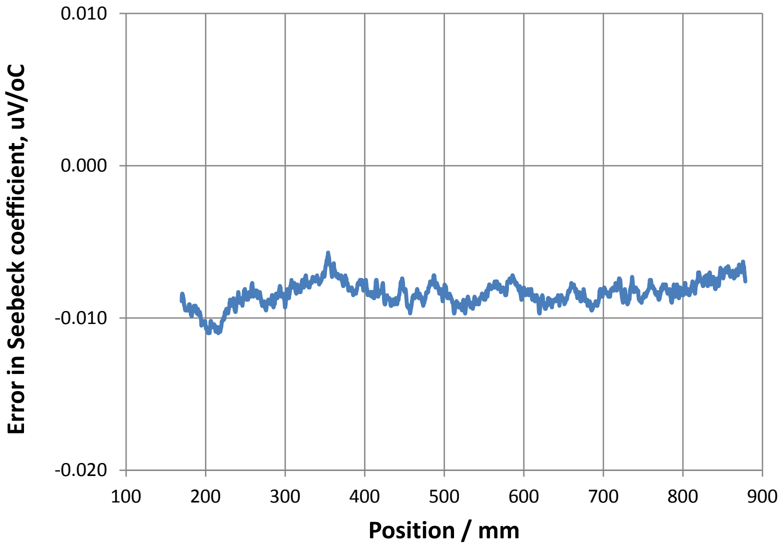

Figure 6: Homogeneity scan of a high-quality Type S thermocouple.

When scanning thermocouples in stirred liquid baths or in fixed-point cells, which have a poorer spatial resolution, it is recommended that the measurements are assumed to be drawn from a rectangular distribution with the distribution width equal to the largest difference found for any two scan measurements. If the test is only performed over a small length of the thermocouple, the largest difference in measured voltage should be taken as half the width of the rectangular distribution [EURAMET 2019].

For example, if we consider the plot between 200 mm and 500 mm in Figure 6 to be the result of a fictitious scan in a liquid bath, the maximum difference is measured to be about 0.005 µV/°C. For a 300 mm length scan, we would assume this difference corresponds to the full width of a rectangular distribution, yielding a standard uncertainty of 0.0025/√3 V, or an equivalent inhomogeneity-related uncertainty of 0.14 °C at 1000 °C. If the scan was carried out over a limited length, say 200 mm to 300 mm, the maximum difference of 0.003 µV/°C is assumed to correspond to the half width of the distribution and a yield a standard uncertainty of 0.003/√3, or an uncertainty contribution of the inhomogeneity at 1000 °C of about 0.17 °C.

In cases where direct measurement of the inhomogeneity is not possible, a Type B assessment of the inhomogeneity is recommended (for new thermocouples only) assuming the following values for the standard uncertainty [Machin et al, 2018]:

- Type K and N: 0.1 % of temperature in °C
- Type R and S: 0.02 % of temperature in °C
- Type B: 0.05 % of temperature in °C
- Au/Pt and Pt/Pd: 0.01 % of temperature in °C
- All other types: 0.25 % of temperature in °C”

Having determined the uncertainty in the Seebeck coefficient we can determine the equivalent uncertainty in temperature. The voltage produced by an inhomogeneous thermocouple is:

$$V_{\mathrm{meas}} = \int_{t_\mathrm{c}}^{t_\mathrm{h}} \left[S_{\mathrm{ref}}(t) + \Delta S(t,x)\right]\left(\frac{dt}{dx}\right)dx\,. \tag{21}$$

where $S_{\mathrm{ref}}(t) + \Delta S(t, x)$ is the Seebeck coefficient $S(t, x)$ at position x along the thermocouple, and dt/dx is the temperature gradient at that location. This equation shows that the inhomogeneity error in any measurement is a complicated function of the temperature gradients and the largely random (see Figure 6) distribution of inhomogeneity errors along the length of the thermocouple.

The measured voltage can be compared to the reference function to give the voltage error caused by the error in the Seebeck coefficient:

$$V_{\mathrm{meas}} - V_{\mathrm{ref}}(t_\mathrm{h}) + V_{\mathrm{ref}}(t_\mathrm{c}) = \int_{x(t_\mathrm{c})}^{x(t_\mathrm{h})} \Delta S(t,x)\left(\frac{dt}{dx}\right)dx. \tag{22}$$

If it is assumed (i) the Seebeck coefficient errors are independent of temperature and a function of position only, i.e., $\Delta S(t,x) = \Delta S(x)$, and (ii) $\Delta S(x)$ is constant over a region where the temperature gradient is imposed, then:

$$\Delta V \approx (t_\mathrm{h} - t_\mathrm{c})\Delta S. \tag{23}$$

If we now divide by the Seebeck coefficient and rearrange (23), we obtain:

$$\frac{\Delta t}{t_\mathrm{h} - t_\mathrm{c}} \approx \frac{\Delta V}{S_{\mathrm{ref}}(t_\mathrm{h})(t_\mathrm{h} - t_\mathrm{c})} \approx \frac{\Delta S(x)}{S_{\mathrm{ref}}(t_\mathrm{h})}\,. \tag{24}$$

This equation shows that the percentage temperature error, for a fixed length of thermocouple, is approximately equal to the percentage error in the Seebeck coefficient. That is, the uncertainty in the temperature measured using a fixed length of thermocouple is related to the standard uncertainty due to inhomogeneity by

$$u_{\mathrm{inhom}}(t) \approx t\frac{u(S)}{S_{\mathrm{ref}}}\,, \tag{25}$$

where it is assumed that the reference junction temperature, t_c, is close to zero. Equation (25) is a useful generalisation for Types R, S, and B, and the pure metal thermocouples Au/Pt and Pt/Pd [Jahan and Ballico 2003a, Webster *et al* 2015a, Webster *et al* 2016, Kim *et al* 2017), Edler and Huang 2020]. Little is known about how inhomogeneity effects scale with temperature for other thermocouple types. It is also unknown how the uncertainty varies with the exposed length of the thermocouple, but we assume that the uncertainty, $u(S)$, is independent of the exposed length.

Equation (25) also applies only to irreversible inhomogeneities; the effects of reversible inhomogeneities are additional and more complicated because they change with use and exposure at different temperatures. However, so long as the thermocouple is annealed prior to use, the conditions of use match the conditions of calibration, and the calibration is performed on rising temperatures, the evolution of reversible effects should be the same in use and calibration, and the effects cancel. For example, Ripple *et al* [Ripple *et al* 2007] describe a comparison of Type K calibrations over the range 100 °C to 1100 °C amongst eleven different laboratories for which the standard deviation of differences between labs was just 2.7 μV, equivalent to about 0.07 °C. Despite Type K exhibiting some of the largest reversible effects observed in thermocouples, tightly controlled procedures applied to wire with a controlled initial thermoelectric state yield very low uncertainties.

The effect of inhomogeneity is to introduce a random error into all thermocouple measurements, both calibration measurements and measurements in use. If we consider only the inhomogeneity errors from the first row of Equation (13) we get,

$$\Delta t_{\mathrm{m,inhom}} = \frac{1}{S(t_{\mathrm{m}})}\left[\sum_{i=1}^{4} F_i(t_{\mathrm{i}})\Delta V_{\mathrm{inhom}}(t_i) - \Delta V_{\mathrm{inhom}}(t_{\mathrm{m}})\right], \tag{26}$$

where $\Delta V_{\mathrm{inhom}}(t_{\mathrm{m}})$ is the inhomogeneity error incurred during the measurement of t_{m}, and $\Delta V_{\mathrm{inhom}}(t_i)$ are the inhomogeneity errors incurred at the calibration temperatures, t_i. If all inhomogeneity effects are statistically independent, and drawn from the same distribution with standard uncertainty, $u(S)$, the uncertainty follows from (23) and (26):

$$u^2_{\mathrm{inhom}}(t_{\mathrm{m}}) = \frac{u^2(S)}{S^2(t_{\mathrm{m}})}\left[\sum_{i=1}^{4} F_i^2(t_m)t_i^2 + t_m^2\right]. \tag{27}$$

In practice, because inhomogeneity errors are fixed features associated with specific parts of the thermocouple wires, measurement uncertainties are correlated if the temperature profiles associated with the different measurements in (27) overlap.

If we assume, firstly, that the length of thermocouple exposed to the temperature gradient is the same for all calibration measurements, which is approximately true for most calibration methods, then the inhomogeneity errors all depend on the same, unchanging Seebeck error, $\Delta S_{\mathrm{cal,inhom}}$, and scale in proportion to the calibration temperatures (Equation (23)). Because the interpolating functions interpolate temperature exactly, $\sum F_i(t_{\mathrm{m}})t_i = t_{\mathrm{m}}$, (Equation (15) with $n = 1$),

$$\Delta t_{\mathrm{m,inhom}} = \frac{t_{\mathrm{m}}}{S(t_{\mathrm{m}})}\left[\Delta S_{\mathrm{cal,inhom}} - \Delta S_{\mathrm{m,inhom}}\right]. \tag{28}$$

The uncertainty in the measurement of an unknown temperature is therefore,

$$u^2_{\mathrm{inhom}}(t_{\mathrm{m}}) = \frac{t_{\mathrm{m}}^2}{S^2(t_{\mathrm{m}})}\left[u^2_{\mathrm{cal,inhom}}(S) - 2ru_{\mathrm{cal,inhom}}(S)u_{\mathrm{tm,inhom}}(S) + u^2_{\mathrm{tm,inhom}}(S)\right], \tag{29}$$

where the correlation coefficient r accounts for correlation arising from overlapping immersion profiles in use and in calibration. Since the magnitude of the uncertainties are the same, $u_{\mathrm{cal,inhom}}(S) = u_{\mathrm{tm,inhom}}(S) = u\ (S)$, the total uncertainty in the measured temperature is:

$$u^2_{\mathrm{inhom}}(t_{\mathrm{m}}) = 2t_m^2\frac{u^2(S)}{S^2(t_{\mathrm{m}})}(1-r). \tag{30}$$

For uncorrelated measurements ($r = 0$) and temperatures measured within the calibration range, (30) gives very similar uncertainties to (27). That is, the effects of correlations between the calibration measurements have little effect on the combined uncertainty. However, when the correction equation is extrapolated outside the calibration points, equation (30) fails to account for the uncertainty amplification. That is, correlation, arising from the use of the same immersion profile for all calibration points, reduces the amplification of inhomogeneity uncertainty caused by extrapolation.

The correlation coefficient depends on the degree of overlap between the lengths of thermocouple exposed to the temperature gradient in use and in calibration. For example, in an *in-situ* calibration, the lengths of exposed thermocouple are nominally identical, so r approaches 1.0 and the uncertainty due to inhomogeneity is mostly eliminated. If there is no overlap in the immersion profiles, $r = 0$, and the uncertainty is a maximum. Note the factor of two in Equation (30) due to the combined effect of the inhomogeneity on the calibration and on the use of the thermocouple.

Where the reference junction is operated at the ice point, consideration must also be given to the effects of inhomogeneities in the thermoelements and copper wires which are exposed to the temperature gradient between ambient and 0 °C. This is especially true when extension or compensating cables are used (See Sec. 4.3.2).

4.1.3. Insulation Breakdown

The electrical resistance of the ceramic insulators used in many thermocouples decreases with increasing temperature (by a factor of about ten for a 200 °C temperature rise) so that, at higher temperatures (above 1500 °C for high-purity alumina), significant electrical shunting may occur between the thermoelements. The effect is greater in MIMS cable than in thermocouples with solid ceramic insulators, because of the longer length of the thermocouples and the larger area of electrical contact between the powder insulator and wires. In poor quality or very thin MIMS thermocouples, chemical diffusion paths can also develop between thermoelements at high temperatures (>900 °C) due to poor or irregular compaction of the insulation material. [Hastings 2012]. Insulation breakdown tends to increase in proportion to immersion, as more of the thermocouple is heated to higher temperatures and increase exponentially with increasing temperature. The effects are hard to detect at room temperature.

Moisture absorbed by the mineral powder insulation near perforations in the sheath of a MIMS cable substantially reduces insulation resistance. However, unlike the other forms of insulation breakdown, the moisture is present at low temperatures and may migrate within the sheath, causing a highly variable and hysteretic response. The presence of moisture can be detected by using a low voltage (100 V) insulation tester to test the insulation between the thermoelements and the sheath. For most thermocouples, the insulation resistance at ambient should exceed 100 MΩ. Wet thermocouples should be treated as faulty and removed from service.

In general, the materials for thermocouples are chosen to ensure insulation breakdown is negligible, so the effect can be neglected in most uncertainty analyses. The exceptions are in long MIMS thermocouples and thermocouples used at very high temperatures. Guidance on upper temperature limits versus diameter for base metal MIMS cables is given in ASTM E 608/E 608M [ASTM 2006].

A detailed numerical model of the effect of insulation breakdown in thermocouples is described in [Roberts and Kollie 1977]. Electrical leakage also causes attenuation of Seebeck voltage and the unwanted mixing of the thermocouple voltage with the thermoelectric voltage produced by the sheath. Equation (13) suggests that calibration can cancel the effects of electrical breakdown, but cancelation requires the temperature profile along the thermocouple to be identical in use and in calibration, which occurs only with the *in-situ* calibration. If the operating conditions during calibration and use are significantly different, the errors should be treated as statistically independent, so the contribution to uncertainty in measured temperature is:

$$u_{\mathrm{ins}}^2(t_{\mathrm{m}}) = \frac{1}{S^2(t_{\mathrm{m}})}\left(u^2(V_{\mathrm{ins,meas}}) + u^2(V_{\mathrm{ins,meas}})\right) . \tag{31}$$

4.1.4. Drift in Thermoelectric State

Ideally, reference thermocouples should be annealed prior to all measurements to minimise the effects of drift in the thermoelectric state, and generally the uncertainty reported on a calibration certificate reflects this assumption. However, it is not always practical or possible to anneal a thermometer prior to every measurement, so users must expect additional uncertainties due to changes in the thermoelectric state. ISO 17025 does not allow the inclusion of uncertainty due to drift in calibration certificates. Instead, the additional uncertainty due to drift must be assessed by the users of calibrated devices according to typical frequency and conditions of usage and observed changes with repeated calibration.

If the thermocouple is fixed in an installation and readings are taken over a long period of time, additional errors arise because of a variety of reversible effects (i.e., removable by annealing), and over longer periods, irreversible effects due to contamination. The drift of thermocouples is commonly described as ‘decalibration’ and may occur even if a thermocouple is properly heat treated, assembled, installed, and calibrated with care.

Figures 7 and 8 show the evolution of thermoelectric changes in a Type S thermocouple versus time, for a range of temperatures up to 900 °C [Webster 2015]. The increase in Seebeck coefficient shown below 650 °C in Figure 7 is due to ordering, and the reduction in Seebeck coefficient between 650 °C and 900 °C is due to rhodium depletion due to oxidation - both effects occur in the alloy thermoelement.

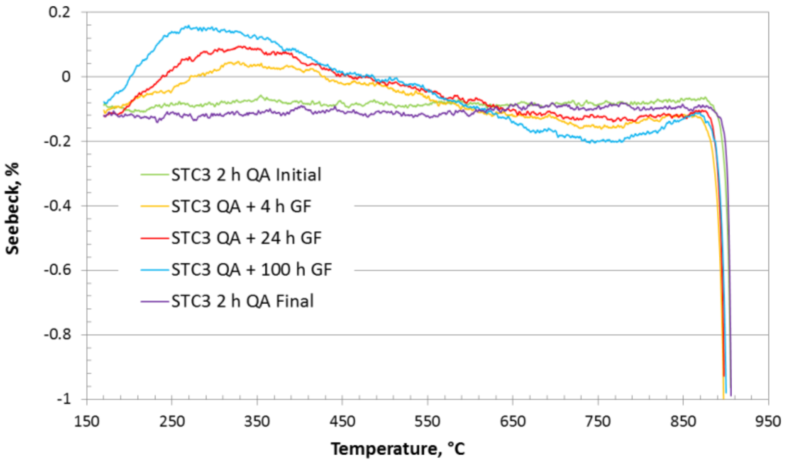

Figure 7: The evolution of reversible inhomogeneities in Type S, in the legend QA indicates a 2 h, 1100 °C quench anneal, and GF indicates gradient furnace aging.

The voltage error due to changes in the Seebeck coefficient is given by the integral:

$$\Delta V = \int_{t_c}^{t_h} \Delta S(t)dt\,. \tag{32}$$

Figure 8 shows the integral of the curves in Figure 7 and indicate the evolution of the measurement error versus operating temperature and time. Note that the ordering effect below 650 °C evolves rapidly and is almost complete after 24 hrs, while the effect of rhodium-oxide depletion above 650 °C occurs more slowly. A reasonable approximation for the maximum error in Type R and Type S is 0.1% of the temperature or 0.5 °C, whichever is larger. These values are typical of the best uncertainties obtained with Types R and S thermocouples when they are used in a fixed installation and not annealed between measurements. No data is available for other thermocouple types, though the effects are expected to be twice as large for Type B, and much less for Au/Pt and Pt/Pd thermocouples.

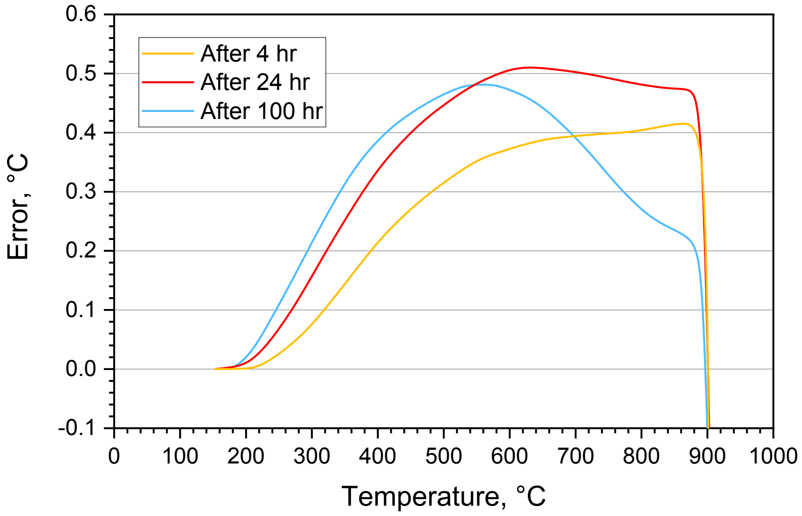

Figure 8: The evolution of ordering and rhodium depletion error versus temperature and time for a Type S thermocouple (from Figure 7).

4.2. Measurement Junction Temperature

4.2.1. Reference Temperatures

Uncertainty evaluations for the uncertainties in the reference temperatures are well covered in other thermometry guides. For fixed points, the uncertainties are reported in the laboratory CMCs (calibration and measurement capability) listed in the ISO 17025 scope of accreditation and/or on the CIPM key comparison database https://www.bipm.org/kcdb/.

Where the temperatures are measured by reference thermometer, the uncertainties are as documented in laboratory procedures and include those reported on the calibration certificates for the thermometer, the meter used to measure the response of the reference thermometer, and uncertainty due to non-uniformity of the calibration media.

4.2.2. Thermal Effects

In common with all contact thermometers, measurement errors arise whenever the sensing element of the thermometer is not at the temperature of interest. Such errors may be caused by heat leaks along the body of the thermocouple due to poor immersion [White 2010], or in response to a rapid temperature change [Augustin and Bernhard 1996, Augustin *et al* 2014], or perhaps due to radiative heating or cooling when the thermocouple is not in isothermal surroundings [Nicholas and White 2001].

According to Equation (13), the net effect of the thermal errors in the measured temperatures (expressed as a voltage), is:

$$S(t_\mathrm{m})\Delta t_\mathrm{m,th} - \sum_i S(t_\mathrm{i})F(t_i)\Delta t_\mathrm{i,th} \,, \tag{33}$$

where $\Delta t_{i,\mathrm{th}}$ are the thermal errors in the calibration measurements and $\Delta t_\mathrm{m,th}$ is the thermal error in the measurement of the unknown temperature (when the thermocouple is used after calibration). If the thermal errors are statistically independent, then the resulting uncertainty (expressed in terms of temperature) is:

$$u_\mathrm{th}^2(t_\mathrm{m}) + \frac{1}{S^2(t_\mathrm{m})}\sum_i S^2(t_\mathrm{i})F_i^2(t_i)u_{i,\mathrm{th}}^2(t_\mathrm{i}) \,. \tag{34}$$

In many situations, the thermal errors have the same sign, so there will be some cancellation, and Equation (34) will overestimate the uncertainty. This happens, for example, when poor immersion causes all measurements to be low. In cases where there are no stray heating effects, a better but still conservative estimate is to use the first term of Equation (34), $u_\mathrm{th}^2(t_\mathrm{m})$, and neglecting the errors in the calibration measurements. The only situations where the error cancellation within Equation (33) is likely to be complete is with an *in-situ* calibration or when comparing or calibrating nearly identical fixed points.

The uncertainties are usually estimated using Type B methods based on subsidiary experiments involving changes in immersion, or changes in temperature outside the nominal isothermal zone where the thermocouples are immersed, or from measurements of the furnace temperature uniformity.

4.3. Reference Junction Temperature

As with the measurement junction, there will be small errors in the reference junction temperature, both thermal errors and errors due to the measurement or realisation of the temperature. The contribution to the measurement error is, from Equation (13):

$$S(t_\mathrm{r})\Delta t_\mathrm{r,th} - \sum_i S(t_i)F(t_i)\Delta t_\mathrm{r,th} \,. \tag{35}$$

In contrast to Equation (33) where the temperature errors arise at different temperatures, the reference junction is maintained in almost identical conditions for all the calibration measurements, so the errors in the reference junction temperature are nearly identical, and since $\sum F_i(t)S(t_\mathrm{r})\Delta t_\mathrm{r,cal} = S(t_\mathrm{r})\Delta t_\mathrm{r,cal}$ according to Equation (15), the measurement error is:

$$\frac{S(t_\mathrm{r})}{S(t_\mathrm{m})}\left(\Delta t_\mathrm{r,m} - \Delta t_\mathrm{r,cal}\right). \tag{36}$$

where $\Delta t_\mathrm{r,m}$ is the reference junction temperature error during use of the thermocouple and $\Delta t_\mathrm{r,cal}$ is the (constant) error during calibration. If the reference junction is prepared in an identical manner for both use and calibration, and operated in a similar environment, the net error due to any error in the reference junction temperature will be close to zero, and the uncertainty negligible.

The result, that most reference junction errors cancel, applies to errors affecting either the reference junction temperature or the reference junction compensation voltage (if used).

If, on the other hand, the reference junctions are maintained by different means for the measurement and the calibration, the errors should be treated as independent and the contribution to the total uncertainty is:

$$\frac{S^2(t_\mathrm{r})}{S^2(t_\mathrm{m})}\left(u^2(t_\mathrm{r,m}) + u^2(t_\mathrm{r,cal})\right). \tag{37}$$

We now consider the different ways that the reference junction and reference junction compensation may be implemented.

4.3.1. Ice Point

The lowest uncertainty reference junction is an ice-point, for which the uncertainty in the realisation is of the order of a few millikelvin, and usually negligible [BIPM 2018]. Additional uncertainty may arise from heat leaks with poor immersion or large diameter metal sheaths.

4.3.2. Extension and Compensating Cable

The Seebeck coefficient of extension or compensating wires is unlikely to match that of the thermoelements exactly, in part because the manufacturer of the two wires may be different, and in part because the manufacturing tolerances on extension and compensating leads are larger than for the thermocouple wires [IEC 2007]. However, so long as the reference junction temperature and the temperature uniformity along the extension and compensating cable are the same for all measurements, then the error will be the same for all measurements, and cancellation effect ensures the effects of the error on measurements is negligible.

Temperature non-uniformity of the nominally isothermal zone enclosing the reference junction can introduce a serious error that may not be reproducible and not cancelled. With normal extension leads, where the extension leads are made from the same materials as the thermoelements the difference in the temperature of the two junctions contributes little error. However, for noble metal thermocouples, the compensating extension leads are copper alloys contributing about 6 µV/°C where the two junctions have different temperatures. Changes in the placement of the reference junction, for example, simply by rotating the sheath in an ice point, will cause changes in the error voltage. A similar error occurs where all thermoelements are terminated at the reference junction with copper lead wires.

Where copper leads or compensating leads are used, some assessment must be made of the likely temperatures difference between the two reference junctions. The larger the temperature gradient across the extension wires, the larger the error caused by this mismatch. Generally, the use of compensating wires should be avoided in high-accuracy measurements, because the manufacturing tolerances of around ±2 °C [IEC 2007] may introduce an unacceptably large uncertainty. If compensating wires must be used, they should be separately calibrated over an appropriate temperature range, e.g., 0 °C to 50 °C, and corrections made if necessary.

4.3.3. Analog Compensation

Where reference junction compensation uses a solid-state electronic device to measure the reference junction temperature, generate the compensating voltage, and add it to the voltage measured by the DVM, there will always be small voltage errors. So long as the junction is maintained in a similar environment for all measurements, then the cancellation effect will render negligible any errors in the compensation voltage. When using a hand-held device, special care is necessary to ensure the reference junction has had time to equilibrate after transport to the measurement site. Care is also required to minimise the effects of local thermal gradients including those caused by the user's body heat when held in the hand.

4.3.4. Digital Compensation

Where reference junction compensation uses an external thermometer to measure the junction and the voltage is added in software, there will be errors. As with the analog compensation, so long as the junction is maintained in a similar environment for all measurements, then the cancellation effect will render the effect on the measurement uncertainty negligible.

4.4. **Voltage Measurement**

4.4.1. Voltmeter

Generally, the performance of modern digital voltmeters (DVM) greatly exceeds the requirements of thermocouple thermometry. A resolution of 0.1 µV and uncertainty of 0.5 µV is sufficient for almost all laboratory measurements, while the best DVMs have uncertainties below 0.1 µV for the entire range of voltages produced by

thermocouples. However, when homogeneity scanning noble metal TCs where the ΔV is small and will be scaled to higher temperatures it is desirable to have an accuracy of around ±50 nV to ensure the uncertainties don't also get scaled up. Most modern digital voltmeters also have auto-zero features, which means that offsets in the readings are negligible. When using a meter without auto-zero, offset errors can be avoided by swapping the leads to the DVM and averaging the two measurements.
Where a single DVM or digital thermocouple indicator is always used with a single thermocouple, then it is not essential to use the corrections determined from an independent calibration. However, an independent calibration is still advised to be sure that the meter performs to specifications and to comply with ISO 17025 [ISO/IEC 2017].

The contribution of the DVM error to the measured voltage is from Equation (13):

$$-\left[\Delta V_{\mathrm{dvm}}(t_{\mathrm{m}})-\sum F_i(t_i)\Delta V_{\mathrm{dvm}}(t_i)\right] \tag{38}$$

The first term, $\Delta V_{\mathrm{dvm}}(t_{\mathrm{m}})$, is the error in the measured voltage during use, while $\sum F_i(t_i)\Delta V_{dvm}(t_i)$ is the polynomial approximating the DVM errors incurred during calibration. If the error introduced by the DVM is well modelled by the thermocouple calibration equation, then the errors largely cancel. Therefore, it is helpful if the same DVM is used for all measurements. The calibration certificate should identify the DVM, the measurement range used, and any other settings that may affect the measurements.

For measurements where a different DVM is used for the calibration and in-use measurements, both DVMs should be independently calibrated at enough points over the calibration range to ensure non-linearity is corrected and the uncertainty properly characterised. The error in DVM indications is usually a simple smooth function well modelled by the thermocouple equation, so the term:

$$\sum_i F_i(t_{\mathrm{m}})\Delta V_{\mathrm{dvm},i}(t_{\mathrm{i}})\,. \tag{39}$$

is a polynomial representing the DVM error. The equivalent temperature error in a measurement is:

$$-\frac{1}{S(t_{\mathrm{m}})}\left[\Delta V_{\mathrm{dvm,meas}}(t_{\mathrm{m}})-\Delta V_{\mathrm{dvm.cal}}(t_{\mathrm{m}})\right]. \tag{40}$$

where the two different DVMs are now distinguished. Therefore, the total uncertainty expressed in the measured temperature is:

$$\frac{1}{S^2(t_{\mathrm{m}})}\left[u^2(V_{\mathrm{dvm,meas}})+u^2(V_{\mathrm{dvm,cal}})\right], \tag{41}$$

where the DVM uncertainties are expressed in terms of the measured voltage rather than the measured temperature. The uncertainty reported on a DVM calibration certificate is often expressed as a fraction of the full-scale range, plus a fraction of the reading. For example, the reported uncertainty might be 1 ppm (part per million) of full scale plus 0.15 ppm of the reading. When used on the 200 mV range to measure a 40 mV voltage, the uncertainty in the measured voltage is 0.2 µV. The uncertainty evaluations for DVMs are normally evaluated for a 90-day period, so additional uncertainty for drift in the DVM readings may be necessary if the calibration is more than 90 days old.

Note that the uncertainty reported on the calibration certificate for the voltmeter should include all effects that occur during normal usage, small offset errors, noise, non-linearity, and round-off errors (finite digital resolution). These terms should not normally appear separately on a thermocouple uncertainty budget.

4.4.2. Electromagnetic Interference

Electromagnetic interference, when it occurs, is often indistinguishable from electronic noise, so the uncertainty is simply characterised by the measured variance,

$$u_{\mathrm{EMI}}^2(t_{\mathrm{m}}) = \frac{1}{S^2(t_{\mathrm{m}})}\left[u^2(V_{\mathrm{EMI,meas}}) + u^2(V_{\mathrm{EMI,cal}})\sum F_i^2(t_{\mathrm{m}})\right]. \tag{42}$$

By design, the effects of EMI should be zero or negligible during calibration and are rarely significant when thermocouples are used in laboratories.

5. Calibration Examples

This section gives three examples of the calibration design and uncertainty analyses for thermocouple calibrations: a reference thermocouple calibrated using fixed points, a reference thermocouple calibrated using another reference thermocouple, and a base metal thermocouple calibrated at a single point. To avoid repetition, a few of the key points are discussed only once so this section should be read as a whole. In most calibrations the total uncertainty is dominated by the uncertainty due to inhomogeneity. However, it is good practice to assess all potential sources of uncertainty to ensure all contributions are as expected, and to ensure confidence in the results by eliminating the possibility of oversight and faulty instruments.

5.1. Example 1: Noble-metal Thermocouple at Fixed Points

Overview. Consider the calibration of a Type S thermocouple used to calibrate other noble-metal thermocouples in the range from 450 °C to 900 °C. To obtain the lowest uncertainties, the calibration uses ITS-90 fixed points to provide the reference temperatures. The three fixed points spanning the range are the zinc, aluminium, and silver points. The thermocouple is assembled with a reference junction for immersion in an ice point and does not have a dedicated DVM. The first part of Table 4 below (key parameters), lists the reference voltages, Seebeck coefficients, and the measured deviations at each of the reference temperatures.

Calibration equation and sensitivity coefficients. The deviation function is the usual cubic polynomial (Equation (2)) with the zeroth-order term set to zero:

$$\Delta V(t) = bt + ct^2 + dt^3. \tag{43}$$

In effect, the ice point is the fourth calibration point but the deviation at 0 °C is set to zero. The remaining three coefficients, b, c, and d are determined from the measured deviations at the three fixed points and will be reported on the certificate. Note that the calibration equation reported on the certificate is the negative of this equation since it must be added to the thermocouple voltage to correct for the deviations, so the signs of the coefficients must be changed.

For the uncertainty analysis, the deviation function is rewritten in the Lagrange form (Equation (8)) with $\Delta V_{\mathrm{ice}} = 0$,

$$\Delta V(t) \approx \Delta V_{\mathrm{Zn}} F_{\mathrm{Zn}}(t) + \Delta V_{\mathrm{Al}} F_{\mathrm{Al}}(t) + \Delta V_{\mathrm{Ag}} F_{\mathrm{Ag}}(t)\ . \tag{44}$$

where the measured deviations are $\Delta V_i = V_{\mathrm{meas}}(t_i) - V_{\mathrm{ref}}(t_i)$, and the interpolating functions are as described in Section 3.1 (Equation (10)) above with $t_1 = 0$ °C:

$$\begin{aligned}
F_{\mathrm{Zn}}(t) &= \frac{t(t-t_{\mathrm{Al}})(t-t_{\mathrm{Ag}})}{t_{\mathrm{Zn}}(t_{\mathrm{Zn}}-t_{\mathrm{Al}})(t_{\mathrm{Zn}}-t_{\mathrm{Ag}})},\\
F_{\mathrm{Al}}(t) &= \frac{t(t-t_{\mathrm{Zn}})(t-t_{\mathrm{Ag}})}{t_{\mathrm{Al}}(t_{\mathrm{Al}}-t_{\mathrm{Zn}})(t_{\mathrm{Al}}-t_{\mathrm{Ag}})},\\
F_{\mathrm{Ag}}(t) &= \frac{t(t-t_{\mathrm{Zn}})(t-t_{\mathrm{Al}})}{t_{\mathrm{Ag}}(t_{\mathrm{Ag}}-t_{\mathrm{Zn}})(t_{\mathrm{Ag}}-t_{\mathrm{Al}})}.
\end{aligned} \tag{45}$$

The fourth interpolating function, $F_{\mathrm{ice}}(t)$, is not required since the deviation is zero.

Operating conditions. The thermocouple is to be used most frequently below 800 °C, so the best reference thermoelectric state is obtained by annealing at 1100 °C followed by a vacancy anneal at 450 °C. The calibrations are carried out in ascending temperatures to minimise the effects of ordering and oxidation on the low-temperature measurements. Because the thermocouple uses a reference junction at the ice point, reference junction compensation is not required, and these terms are omitted from the uncertainty budget.

Uncertainty contributions. The most significant contributions to uncertainty are discussed below in order of significance and summarised in Table 4.

- Inhomogeneity: The standard uncertainty due to homogeneity was assessed (after annealing) using a homogeneity scanner and found to be 0.020%. The inhomogeneity is assumed to be normally distributed.
- Thermal effects: The various thermal effects associated with the immersion of the thermocouple in the fixed-point cells were evaluated using the results of subsidiary experiments in the laboratory quality system in the laboratory calibration and measurement capabilities (CMC). The uncertainty is estimated to be about 0.01 °C, and the effects are assumed to be normally distributed.
- Reference temperatures: While the temperatures of the fixed points are defined, there are uncertainties associated with their realisation, due mainly to impurities and hydrostatic pressure effects. These uncertainties, which are of the order of millikelvin, are recorded in the laboratory quality system in support of their CMC. The errors are assumed to be normally distributed.

- Digital Voltmeter: The uncertainty recorded on the calibration certificate for the DVM when operated on the 100 mV range is 9 ppm (parts per million) of full scale plus 3 ppm of the reading. The errors are assumed to be normally distributed.
- Reference junction: The ice point reference junction is easily realised with uncertainties below a few millikelvin. The errors are assumed to be normally distributed. Because an ice point is used, there is no reference junction compensation or compensating leads required.

The remaining uncertainties are negligible.

Once the uncertainties have been assessed and the table has been filled in, the columns are summed in quadrature to give the uncertainties in terms of voltage. Note that the errors affecting the temperature references are added separately (in degrees Celsius) from the errors affecting the measured voltages (in microvolts). Once the uncertainties in the measured voltages and in the realisations of the temperatures have been determined the combined uncertainty in a measured temperature is calculated as

$$u(t)=\frac{1}{S(t)}\left[\sum_{i=1}^{3}F_i^2(t)\left[u^2(V_i)+S^2(t_i)u^2(t_i)\right]+u^2(V)\right]^{1/2} . \qquad (46)$$

The last uncertainty term in Equation (46), $u(V)$, is the sum of the terms arising in use, including (see Table 4), the thermal errors associated the measurement of the unknown temperature, the effect of inhomogeneity in use, the user's digital voltmeter, and the user's realisation of the ice point reference junction. Generally, the user can easily determine all these contributions except the inhomogeneity. It is therefore helpful to users if the calibration laboratory includes the inhomogeneity in the uncertainty and the certificate guides the user to add their estimates of uncertainties for the additional sources of uncertainty: the thermal errors, the DVM uncertainty, the reference junction temperature uncertainty.

Figure 9 plots Equation (46) for the combined uncertainty. There are several observations to be drawn from Figure 9 and Table 4. Firstly, as is typical for most thermocouple calibrations, the total uncertainty is almost entirely due to inhomogeneity. Secondly, there is an increase in uncertainty with extrapolation outside the 420 °C to 960 °C range of the three calibration points. The uncertainty decreases below 200 °C because the deviation equation must pass through zero at the ice point (the deviation at 0 °C is set to zero by choosing $a = 0$ in Equation (2)). If the thermocouple was to be used below 400 °C, it would be better to include a calibration point at the tin point (231.928 °C) and not require the deviation function to be zero at 0 °C ($a \neq 0$ in Equation (43)).

Reporting. The calibration certificate reports the results in the form of Equation (43) with the coefficients assigned the numeric values determined from the measured deviations. For example, the report might state that "The temperature indicated by the thermocouple is inferred from the Type S reference function with the measured voltages, $V_{\text{meas}}(t)$ corrected using the equation:

$$V_{\mathrm{corr}}(t) = V_{meas}(t) + \Delta V_{corr}$$

where,

$$\Delta V_{corr} = At + Bt^2 + Ct^3 \text{ ,}$$

and

$A = +5.69 \times 10^{-3}$ μV/K,
$B = -2.83 \times 10^{-6}$ μV/K^2,
$C = +1.06 \times 10^{-8}$ μV/K^3 ."

Note that the correction equation has the opposite sign to the deviation function, since it must correct for the deviation, and hence $A = -b, B = -c, C = -d$, where *b*, *c*, and *d*, are the coefficients of the deviation function, Equation (43). The number of significant figures reported should be sufficient to avoid roundoff error.

The reported uncertainty need not be as complicated as Equation (46). Indeed, so long as (i) the uncertainty due to inhomogeneity dominates, (ii) the equation is not used for extrapolation, and (iii) the calibration points are well spaced, then a line may be a satisfactory approximation. Figure 9 also shows the line $u(t) = 0.08 + 0.00022t$, which is satisfactory for the range 400 °C to 1000 °C.

The certificate should include a note explaining the uncertainty. For example, “The reported uncertainty is the standard uncertainty in measured temperature over the range 420 °C to 960 °C, corrected with the calibration equation, and including the effects of thermocouple inhomogeneity. It excludes the uncertainties due to the user’s voltmeter, uncertainties due to thermal effects caused by furnace non-uniformity and poor immersion in use, and uncertainties in the reference junction temperature in use.” The certificate should also report the measurement conditions, the annealing procedure, and the fact that an ice point was used.

Table 4. A summary of the uncertainty contributions for a fixed-point calibration of a Type S thermocouple. The upper section summarises key parameters in the calibration. The middle section summarises the contributions to uncertainties in the realised temperatures, while the lower section summarises the contributions to the measured voltages. All uncertainties are expressed as standard uncertainties. See text for detailed explanation of the assessments. The input data is in the shaded cells.

Key parameters	t_{ice} **(reference junction)**	t_{zinc}	$t_{\mathrm{aluminium}}$	t_{silver}
Calibration temperatures, t_i	0 °C	419.527 °C	660.323 °C	961.780 °C
Reference voltage, $V_{\mathrm{ref}}(t_i)$	0 μV	3446.9 μV	5860.1 μV	9148.4 μV
Seebeck coefficient, $S_{\mathrm{ref}}(t_i)$	5.40 μV/ °C	9.64 μV/ °C	10.40 μV/ °C	11.42 μV/ °C
Measured deviation, $V(t_i) - V_{\mathrm{ref}}(t_i)$	Assumed to be zero	+1.8 μV	+5.5 μV	+11.2 μV

Source of Uncertainty	**Assessment data**	t_{m}	t_{zinc}	$t_{\mathrm{aluminium}}$	t_{silver}
Inhomogeneity	Homogeneity scan, 0.020% of $t \times S(t)$	$0.0002t_{\mathrm{m}}$	0.084 °C	0.132 °C	0.192 °C
Reference temperatures	Laboratory procedure and CMC	0	0.002 °C	0.003 °C	0.004 °C
Thermal effects - immersion	Immersion experiments	0 (user to assess)	0.010 °C	0.010 °C	0.010 °C
Total of temperature terms $u(t_i)$	$u(t_i)$		**0.085 °C**	**0.132 °C**	**0.193 °C**
Voltmeter (100 mV range)	1 yr Cal. Cert. 9 ppm range+3 ppm reading	0 (user to assess)	0.91 μV	0.92 μV	0.93 μV
Reference junction (ice point)	Laboratory procedure and CMC, 10 mK	0 (user to assess)	0.03 μV	0.03 μV	0.03 μV
Total of voltage terms $u(\Delta V_i)$	$u(\Delta V_i)$	0 (user to assess)	**0.91 μV**	**0.92 μV**	**0.93 μV**
Combined Uncertainty, $u_{\mathrm{cal}}(V)$	$\left[u^2(\Delta V_i) + S^2(t_i)u^2(t_i)\right]^{1/2}$	$u(V)$	**1.22 μV**	**1.66 μV**	**2.39μV**

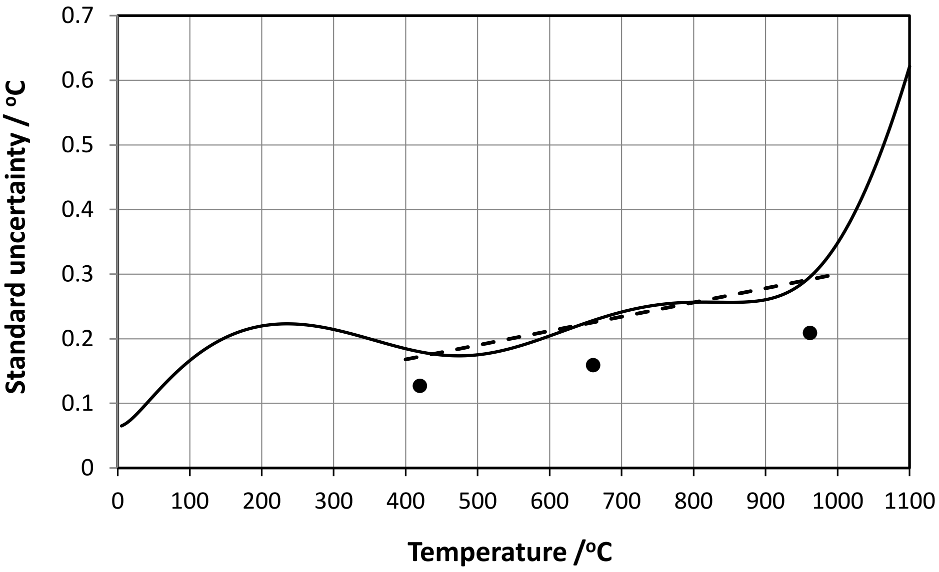

Figure 9: The total standard uncertainty (solid line) for a Type S thermocouple calibrated at the zinc, aluminium, and silver fixed points. The dotted line is a linear approximation for the range 400 °C to 1000°C. The points show the contribution of calibration uncertainties at the fixed points.

5.2. Example 2: Noble-metal Thermocouple by Comparison

Overview. Consider the calibration of a new Type S reference thermocouple used to calibrate base-metal thermocouples over the range from 500 °C to 1100 °C. The thermocouple has its own dedicated voltmeter/indicator reading directly in degrees Celsius and a reference junction at ambient temperature. The calibration is carried out by comparison with another Type S thermocouple previously calibrated using fixed points. The junctions of the two thermocouples are welded together and immersed into a tube furnace and compared at four points: 500 °C, 700 °C, 900 °C and 1100 °C. The first part of Table 5 below, lists the measured temperatures, voltages, and Seebeck coefficients.

Calibration equation. The calibration equation is a cubic polynomial, and the sensitivity coefficients are as described in Section 3.

Uncertainty contributions.

- Inhomogeneity. The laboratory does not have a homogeneity scanner, so assumes (Type B uncertainty assessment) that the inhomogeneity in the thermocouple under calibration is typical for a new Type S thermocouple, i.e., 0.03% of emf (or a thermocouple that has never exceeded 1100 °C and has been annealed at 1100 °C followed by a vacancy anneal at 450 °C). The inhomogeneity errors are assumed to be normally distributed.
- Reference thermocouple. This uncertainty is taken from the calibration report for the reference thermocouple. The errors are assumed to be normally distributed.
- Drift in the reference thermocouple. The laboratory operates full time and only anneals the reference thermocouple at the beginning of some weeks. A

Type B assessment of the drift of the thermocouple from the reference state over periods of a few days suggests that the changes in state are responsible for uncertainty of about 0.3 °C (See Figure 7). Because the drift is linear, the error is assumed to be drawn from a uniform distribution.

- Thermal effects. Measurements of the furnace uniformity and experiments with rotated pairs of thermocouples welded together shows that thermal effects are only a few tenths of a degree and rise in proportion to the temperature. The errors were found to be approximately uniformly distributed.
- Reference junction. The specification for the reference junction is that any errors are less than 0.2 °C for all specified ambient temperatures. Assume this figure is expanded uncertainty with a coverage factor of 2, leading to a standard uncertainty of 1 µV for the reference junction error.
- The voltmeter. The calibration certificate for the voltmeter used to measure the reference thermocouple reports a standard uncertainty of 4 ppm of range (200 mV) plus 2 ppm of reading, approximately 1 µV for all measurements here. The DVM errors are assumed to be normally distributed.

The remaining uncertainties are negligible, as summarised in Table 5. As discussed in Section 4, the voltmeter and its reference junction are always part of the measurement system and are calibrated with it. The measured calibration equation will include therefore corrections for any error caused by the voltmeter or the reference junction compensation. The uncertainties associated with these two components relate to the drift and repeatability. All other uncertainties associated with the use of the thermocouple are outside the control of the calibration lab and not a part of the measuring instrument (thermocouple plus DVM).

Figure 10 plots the combined standard uncertainty in temperatures measured with the calibrated thermocouple, including the uncertainty due to inhomogeneity in use, the DVM in use, and the reference junction in use. The curve for the total uncertainty reinforces previous observations about the increase in uncertainty with extrapolation beyond the calibration range. The dotted line on the plot is the linear approximation $u(t) = 0.3\ °\mathrm{C} + 0.00035t$.

Reporting. The calibration certificate reports, as before "The temperature indicated by the thermocouple is inferred from the Type S reference function with the measured voltages, $V_{\mathrm{meas}}(t)$ corrected using the equation:

$$V_{\mathrm{corr}}(t) = V_{meas}(t) + \Delta V_{corr}$$

where,

$$\Delta V_{corr} = A + Bt + Ct^2 + Dt^3\,,$$

and

$$A = -a = -\,6.25\ \mu\mathrm{V},$$
$$B = -b = +6.89\times10^{-2}\ \mu\mathrm{V/K},$$
$$C = -c = -7.94\times10^{-5}\ \mu\mathrm{V/K}^2,$$
$$D = -d = +2.52\times10^{-8}\ \mu\mathrm{V/K}^3\,.$$

The certificate should include a note explaining the uncertainty: "The reported uncertainty is the standard uncertainty in temperature measurements over the range 500 °C to 1100 °C, corrected with the calibration equation, and including the effects of thermocouple inhomogeneity, the DVM and the reference junction. It excludes uncertainties due to thermal effects in use".

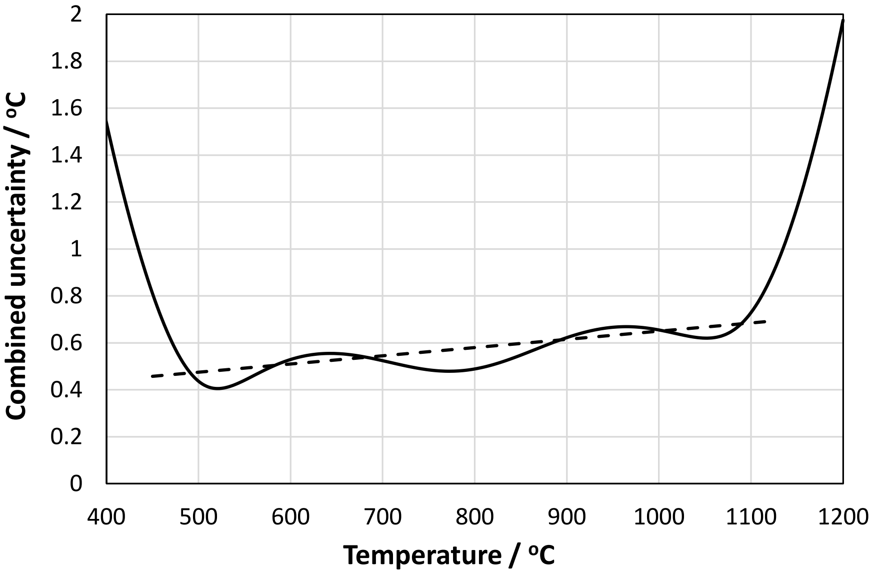

Figure 10: The combined standard uncertainty (solid line) for a Type S thermocouple calibrated at four temperatures using a reference thermocouple. The dashed line is an approximation.

Table 5. A summary of the uncertainty contributions for a comparison calibration of a Type S thermocouple.

Key parameters	**Nominal temperature**	t_1	t_2	t_3	t_4
Calibration temperatures according to reference thermocouple, t_i		501.3 °C	700.8 °C	900.2 °C	1099.6 °C
Reference voltage, $V_{\text{ref}}(t_i)$		4246.2 µV	6283.7 µV	8451.5 µV	10751.8
Seebeck coefficient, $S_{\text{ref}}(t_i)$		9.90 µV/ °C	10.53 µV/ °C	11.21 µV/ °C	11.83 µV/ °C
Measured deviation, $V(t_i) - V_{\text{ref}}(t_i)$		-11.5 µV	-11.7 µV	-9.8 µV	-7.0 µV

Source of Uncertainty	**Assessment data**	t_m	t_1	t_2	t_3	t_4
Inhomogeneity	Published data, 0.030% of t	$0.0003t_m$	0.15 °C	0.21 °C	0.27 °C	0.33 °C
Reference temperatures	Calibration certificate, 0.1 °C+0.0003t	-	0.25 °C	0.31 °C	0.37 °C	0.43 °C
Drift of reference	Published data (e.g., Figure 7)	-	0.17 °C	0.17°C	0.17 °C	0.17 °C
Thermal effects	Immersion experiments	-	0.1 °C	0.15 °C	0.2 °C	0.25 °C
Total of temperature terms $u(t_i)$	$u(t_i)$		**0.352 °C**	**0.438 °C**	**0.528 °C**	**0.621 °C**
Reference junction	Manufacturer's specification	0.1 °C	1.0 µV	1.0 µV	1.0 µV	1.0 µV
Voltmeter (200 mV range)	1 yr Cal. Cert. 4 ppm range+2 ppm reading	1.0 µV	1.0 µV	1.0 µV	1.0 µV	1.0 µV
Total of voltage terms $u(\Delta V_i)$	$u(\Delta V_i)$	1.0 µV	**1.41 µV**	**1.41 µV**	**1.41 µV**	**1.41 µV**
Combined Uncertainty, $u_{\text{cal}}(V)$	$\left[u^2(\Delta V_i) + S^2(t_i)u^2(t_i)\right]^{1/2}$	-	**3.8 µV**	**4.8 µV**	**61 µV**	**7.5 µV**

5.3. Example 3: Base-metal Thermocouple by Comparison

A MIMS format Type K thermocouple to be used as a working thermometer is calibrated at a single point near 1000 °C. The thermocouple is one of a batch of nominally identical thermocouples made from the same batch of MIMS cable. The calibration is performed to confirm that the thermocouple conforms with the Type K definition and tolerances, and to determine the deviation at 1000 °C, which will be applied as a correction to the remaining thermocouples in the batch.

Calibration equation and sensitivity coefficients. The calibration equation in this case assumes that a single constant correction can be applied in the vicinity of the working temperature of the thermocouple, so the deviation function is,

$$\Delta V(t) = a \,.$$

The value of a is determined by a single comparison with the reference thermocouple at the calibration temperature,

$$\Delta V(t) = \Delta V(t_{\mathrm{cal}}) \ \ .$$

The mathematical expressions for the sensitivity coefficients (Equation (13)) are very much simplified because there is a single interpolating function, $F(t) = 1$, so the summation signs and interpolating functions in Equation (13) can be ignored.

Operating conditions. The thermocouple is to be used near 1000 °C and is one of several thermocouples linked via a scanner (multiplexer) to the voltmeter. The voltmeter is submitted to the laboratory with the thermocouple, as a single working unit. The voltmeter operates with a reference junction at ambient temperature with reference junction compensation. In the calibration laboratory, the reference junction is close to 20 °C. In use, the reference junction may be at any temperature between 10 °C and 40 °C depending on the weather and wind direction.

Uncertainty contributions.

- Inhomogeneity: The homogeneity of the thermocouple was assessed as received and found to be about 0.2%. Most base-metal thermocouples are sold un-annealed having been drawn into wire, i.e., a work-hardened state. Over the first minutes to hours of use, the hottest parts of the wire will rapidly anneal and ordering effects around 400 °C will commence, causing rapid drift in the thermocouple response of perhaps several degrees Celsius. After consultation with the user, the laboratory has agreed to calibrate the thermocouple following a minimum of two hours exposure at 1000 °C, so that the thermocouple has been partially conditioned for use at 1000 °C and the calibration reflects the expected usage of the other thermocouples in the batch (normal distribution).
- Reference Thermocouple. The uncertainty is as reported on the calibration certificate (normal distribution).
- Drift in reference thermocouple. The calibration laboratory routinely calibrates base-metal thermocouples, so does not require the low uncertainties that would necessitate frequent annealing of the reference thermocouple (rectangular distribution).
- Thermal effects. To avoid contamination of the reference thermocouple from the sheaths of base-metal thermocouples, the reference thermocouple is used within a 10 mm diameter ceramic sheath. The very different immersion characteristics of the reference thermocouple and thermocouple under test mean that there may be temperature differences as large as 1 °C between the two. An uncertainty of 0.5 °C is assessed (rectangular distribution).

- Voltmeter. The same voltmeter is used for measurement and calibration, so the uncertainty is taken to be zero (see Section 4.4.1) (normal distribution).
- Because of the changing ambient temperature, there is likely to be some uncertainty introduced by the sensitivity of the reference junction to ambient temperature. The voltmeter manufacturer specifies that the reference junction compensation is accurate to within 0.5 °C for all temperatures between 0 °C and 50 °C, so an uncertainty of 0.25 °C is assessed (normal distribution).

All other uncertainties are negligible, as summarised in Table 6. Note that all the uncertainties are evaluated at a single temperature, and can be expressed in terms of temperature, and added as a temperature.

Table 6. A summary of the uncertainty contributions for a calibration of a Type K thermocouple.

Key parameters	
Calibration temperatures, t_i	1000 °C
Reference voltage, $V_{\mathrm{ref}}(t_i)$	41276 μV
Seebeck coefficient, $S_{\mathrm{ref}}(t_i)$	39.0 μV/ °C
Measured temperature deviation, $t_{\mathrm{ref}} - t_i$	+4.7 °C

Source of Uncertainty	**Assessment data**	t_{m}	t_{cal}
Reference temperatures	Calibration certificate, 0.25 °C+0.00035t	-	0.6 °C
Drift in reference	Published data (e.g., Figure 6)	-	0.3 °C
Thermal effects	Immersion experiments	-	0.3 °C
Inhomogeneity	Published data, 0.20% of t	2 °C	2 °C
Reference junction temperature		0.25 °C	-
Total of temperature terms $u(t_i)$	$u(t_i)$	**2.0 °C**	**2.1 °C**

Reporting. The certificate could report that the correction to the Type K reading at 1000 °C is –4.7 °C and that the standard uncertainty in the corrected reading is 2.9 °C. The problems of reversible effects in Type K, combined with the unknown thermoelectric state of the batch of thermocouples means that the certificate should also clearly state the identification for the batch and the thermal pre-treatment applied to the thermocouple, in addition to uncertainties due to thermal effects.

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