HOW ACCURATE ARE THOSE THERMOCOUPLES?

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INTRODUCTION

Inevitably, during any QC Audit of the Laboratory's calibration procedures, the question of thermocouple accuracy is raised. The measurement of temperatures with thermocouples, *Thermoelectric Thermometry*, is one of the most often used laboratory and manufacturing measurements, yet is by far the least understood. Even experienced researchers who have used these techniques for years rarely have a true grasp of how these devices operate and what the sources of error are.

The following discussion has been organized into three levels of complexity. However, they all make the same points. The reader is encouraged to follow these explanations to a level at which s/he is comfortable, and is referred to the American Society for Testing and Materials (ASTM) *Manual On The Use of Thermocouples In Temperature Measurement*, Fourth Edition, sponsored by ASTM Committee E20 on Temperature Measurement, from whence all quoted sections of this document were taken.

CONCLUSIONS

While normally presented at the end of a discussion, I have moved the conclusions to this position, to assist those unfamiliar with the theories and mathematics of thermodynamics.

The various levels of discussion which follow will show the reader that, assuming that the data acquisition system utilized to measure the thermocouple signal is calibrated and accurate, the most important property of a thermocouple is the purity and composition of the wires making up both legs of the circuit, *not* the condition of the thermojunction itself. As long as the two legs of the circuit are connected electrically at the temperature measuring point, the thermocouple will read as accurately as the quality of its wires allows.

The thermocouple wires utilized by many laboratories are purchased as Special Limits of Error from the manufacturer. As a check on the quality (purity of materials) of these thermocouples, the manufacturer selects specimens from both ends of each Lot Number purchased and performs accuracy checks at five temperature levels, using measuring equipment of appropriate accuracy and traceability to N.I.S.T. OPL's Quality Assurance Department performs routine audits of the thermocouple manufacturer's calibration procedures, to assure the accuracy calibrations are being performed satisfactorily. Other than a functionality check (to ensure electrical continuity across the thermojunction), no other assurance of the accuracy of the thermocouples is deemed necessary.

The remainder of this document will consist of an increasingly robust description of thermocouples, how they work, and why the wire purity is so important.

LEVEL ONE

BRIEF OVERVIEW OF THERMOCOUPLE BEHAVIOR

The very simplest description of how a thermocouple works is that it consists of an electrical circuit that produces a voltage that can be used as a measure of temperature. This circuit must consist of two different, electrically-conductive materials electrically joined at one end. When the temperature at the joined end of these two materials is different than the temperature at the open ends (at which an accurate voltmeter is attached), then a voltage difference will exist (which will be measured by the voltmeter, and can be used to determine the temperature difference between the two locations).

The voltage which is generated at the “measurement” end of the thermocouple circuit is developed due to the difference in temperature at each end of **each wire**. The voltage difference is not, as is often erroneously believed, developed across the junction of different metals. This voltage, which is developed at opposite ends of each wire due to the fact that it’s two ends are at different temperatures, is dependent on the type and purity of the wire’s material.

If both “legs” of the thermocouple circuit were made up of identical materials, then an identical voltage would be developed across each, and the net voltage measured by the voltmeter would be zero. However, if the wires are made up of different materials, joined at one end only, then the measuring device will, in effect, be measuring the difference in voltage developed across both wires, which will not be zero, since the different materials generate different (but known) voltages.

Assuming that the ends at which the two different wires are joined are in good electrical contact and that no measuring error is introduced through incorrect terminals or voltage measurement techniques, then the accuracy of the thermocouple will be a simple function of the purity of each of the two materials (normally wires).

Voltage tables exist which relate the voltage developed across thermocouple wires of precisely known material compositions. The more accurately the purity of each wire’s material is known, the more accurately the temperature difference between the two ends of the thermocouple system can be determined. Thermocouple wire is manufactured using many different pairs of materials, depending upon the accuracy, range and durability required. Within a given thermocouple “Type,” (standardized pair of dissimilar materials), various levels of purity (and hence accuracy) can be purchased. Similarly, the electrical insulation surrounding these pairs of wires (thermocouple wire is normally purchased as a two-wire system, with an electrical insulation around each conductor and an overall wrap to keep them together) is available in a wide range of materials, depending upon the required resistance to temperature, water or caustic materials or conditions.

For general laboratory use, the Type K (Chromel-Alumel) thermocouple is utilized. Type K thermocouples are recommended for use in an oxidizing or completely inert atmosphere over the temperature range of -330 to 2300°F. Type K thermocouples are made up of one wire consisting of 90% nickel/10% chromium and the other containing 90% nickel/5% aluminum and silicone. This thermocouple type (like most other types) is available in two grades of purity: Standard Limits of Error (the greater of ± 2.2°C or ± 0.75%); and, Special Limits of Error (the greater of ± 1.1°C or 0.4%). All thermocouple wire purchased and used by Omega Point Laboratory is of the Special Limits of Error quality. Wires of higher purity are not commercially available. Thermocouples, then, cannot be expected to produce better accuracy than the purity of their materials dictates. At best, a Type K thermocouple (of Special Limits of Error) will yield the following accuracy:

Actual Temperature, °C (°F)	**Maximum Accuracy, ±°C (±°F)**
0 (32)	1.1 (2.0)
100 (212)	1.1 (2.0)
200 (392)	1.1 (2.0)
300 (572)	1.2 (2.2)
400 (752)	1.6 (2.9)
500 (932)	2.0 (3.7)
750 (1382)	3.0 (5.4)
1000 (1832)	4.0 (7.2)
1250 (2282)	5.0 (9.0)

LEVEL TWO

A CLOSER VIEW OF THERMOCOUPLE BEHAVIOR

The voltage which develops across a thermocouple as a function of the temperature of the sensing portion of that circuit has been named the Seebeck emf. “The Seebeck emf occurs within the legs of a thermocouple. It does not occur at the junctions of the thermocouple as is often asserted nor does the Seebeck emf occur as a result of joining dissimilar materials as is often implied.

In grossly simplified terms, a conducting material is represented as containing a collection of free conduction electrons distributed over the volume of the body and each is associated with its electrical charge. In a statistical sense, the electrons, and so the charges, are distributed uniformly throughout the volume if the body is homogeneous, isothermal, and not subjected to a significant magnetic field or significant mechanical load.

However, the distribution of the relative density of charge throughout a particular conductor depends on the temperature distribution. If the body temperature is nonuniform, charge is concentrated in some regions and rarified in others. The uneven charge distribution produces a corresponding nonuniform equilibrium distribution of electrical potential throughout the body. For example, if the body is in the form of a homogeneous slender wire a nonuniform longitudinal temperature distribution results in a variation of electrical potential along the wire. If the two ends of the wire are at different temperatures there necessarily will exist a net potential difference between the endpoints. Any emf produced only by nonuniform temperature distribution in such a homogeneous electrically conducting body is the Seebeck emf.

If the free ends of that wire are then joined electrically to form a circuit the temperatures of those joined ends are forced to be the same and, following a very brief transition interval, the charge distribution will equilibrate to a new static distribution. Only during the very brief interval while equilibrium is being established is there statistically a net motion of the charge that constitutes a transient Seebeck current. In the closed nonisothermal homogeneous material circuit at equilibrium there is a nonuniform distribution of charge but no net charge motion and, therefore, no steady-state Seebeck current. The transient temperature state is not well addressed by equilibrium thermodynamics, and the equilibrium thermoelectric state in a single homogeneous circuit is of only incidental thermodynamic interest and is of no benefit in thermometry.

If two slender homogeneous dissimilar conducting materials are joined only at one of their ends and the junction and terminals are maintained at different temperatures then there persists a continual potential difference between the ends of each of the legs (*but not current* so neither Thomson nor Peltier effects occur) and generally there will be a difference between the net potentials between the separate ends of the two legs. It is this net equilibrium open-circuit Seebeck potential difference that is used in thermometry.

LEVEL THREE

A MATHEMATICAL VIEW OF THERMOCOUPLE BEHAVIOR

The following discussion of the mathematics behind the thermocouple was taken from the ASTM Manual on The Use of Thermocouples in Temperature Measurement, Fourth Edition, as previously referenced.

“Thermoelectric characteristics of an individual material, independent of any other material, by tradition are called *absolute*. These actual characteristics are measured routinely though not in a thermocouple configuration. If any individual electrically conducting material, such as a wire is placed with one end at any temperature T_a, and the other at a different temperature, T_b, a Seebeck emf, E_σ actually occurs between the ends of the single material. If T_a is fixed at any arbitrary temperature, such as 0 K, any change in T_b produces a corresponding change in the Seebeck emf. This emf in a single material, independent of any other material, is called the *absolute Seebeck emf*.

With the temperature of endpoint *a* fixed, from any starting temperature of endpoint *b*, a small change, ΔT, of its temperature, T_b, results in a corresponding increment, ΔE_σ , in the absolute Seebeck emf. The ratio of the net change of Seebeck emf that results from a very small change of temperature to that temperature increment is called the *Seebeck coefficient*. This is the measure of thermoelectric sensitivity of the material. Where the sensitivity is for an individual material, separate from any other material, it is called the *absolute Seebeck coefficient*. . .

We designate the thermoelectric sensitivity, or Seebeck coefficient, by, σ. As this coefficient is not generally a constant, but depends on temperature, we note the dependence on temperature by σ(T). Mathematically, this coefficient is defined by the simple relation

$$\sigma(T) = \lim_{\Delta T \to 0} \frac{\Delta E_\sigma(T)}{\Delta T}$$

where ΔT is the temperature difference between ends of a segment, *not* the change of average temperature of the segment. On a graph of E_σ versus T, σ(T) corresponds to the local slope of the curve at any particular temperature, T.

A thermoelectrically homogeneous material is one for which the Seebeck characteristic is the same for every portion of it. For a homogeneous material, the net Seebeck emf is independent of temperature distribution along the conductor. For any particular homogeneous material, the endpoint temperatures alone determine the net Seebeck voltage. Note, however, that this relates only to a homogeneous material. . .

The relation between absolute Seebeck emf and temperature is an inherent transport property of any electrically conducting material. Above some minimum size (of submicron order) the Seebeck coefficient does not depend on the dimension nor does it depend on proportion, cross-sectional area, or geometry of the material.

The basic mathematical relationship above is called the Fundamental Law of Thermoelectric Thermometry, and is expressed in a form that states the same fact in an alternate way

$$dE_{\sigma} = \sigma(T)\, dT$$

It is very important to recognize that it is merely this simple relation that must be true if the Seebeck effect is to be used in practical thermometry. For thermometry, nothing more mysterious is required than that Seebeck emf and the temperatures of segment ends be uniquely related. That the relation is actually true for practical materials is confirmed by both experiment and theory.

The equation above can be expressed in yet another useful form that expresses the absolute Seebeck emf of an individual material

$$E_{\sigma}(T) = \int \sigma(T)dT + C$$

This indefinite integral defines the absolute Seebeck emf only to within the arbitrary constant of integration, C. It definitely expresses the relative change of voltage that corresponds to a change of temperature condition, but it does not define the absolute value of that emf. To remove this uncertainty, it is necessary to establish one definite temperature condition.

The absolute Seebeck emf can be conveniently referenced to 0 K. Therefore, the net absolute Seebeck emf between the two endpoints of any homogeneous segment with its endpoints at different temperatures is

$$E_{\sigma} = \int_{0}^{T2} \sigma(T)dT - \int_{0}^{T1} \sigma(T)dT$$

or,

$$E_{\sigma} = \int_{T1}^{T2} \sigma(T)dT$$

Distinct from the indefinite integral above, this final definite integral unambiguously represents the net absolute Seebeck emf across any homogeneous nonisothermal segment. It simply adds all the contributions from infinitesimal temperature increments that lie between two arbitrary temperatures. This equation also establishes the thermoelectric sign convention. The absolute Seebeck coefficient is positive if voltage measured across the ends of the segment would be positive with the positive probe on the segment end with the higher temperature. The result of integration is merely the difference of absolute Seebeck emfs for the two endpoint temperatures

$$E_\sigma = E_\sigma(T_2) - E_\sigma(T_1)$$

as directly obtained from a table, a graph, or from the definite integral above. The net Seebeck emf is found in this simple way regardless of the intermediate values along the element between those two temperatures and also regardless of the common reference temperature chosen. Fortunately, while it may be convenient to refer the Seebeck emf to 0 K, the reference temperature can be any value.

It helps to realize that any segment or collection of dissimilar segments, regardless of inhomogeneity, contributes no emf so long as each is isothermal. Any homogeneous segment with its endpoints at the same temperatures contributes no net Seebeck emf regardless of temperature distribution apart from its endpoints.

Any slender *inhomogeneous* conductor can be treated as a series-connected set of Seebeck cells, each segment of arbitrary length, each segment essentially homogeneous, each segment with its own $\sigma(T)$ relation. Effectively, an inhomogeneous conductor is a Seebeck battery (or pile) composed of series-connected Seebeck cells with different characteristics that must be considered individually. If the distribution of Seebeck coefficient and temperature along any conductor were known the net Seebeck emf across it could be calculated easily from the equations above. Ordinarily, this distribution information is not known. Unfortunately, for any unknown temperature distribution around a circuit, if only the net emf from an inhomogeneous conductor is known, neither the temperature distribution, the distribution of Seebeck coefficient, nor the endpoint temperatures can be deduced. It is for this reason that an inhomogeneous thermocouple cannot be used for accurate thermometry. Recognize that *thermoelectric homogeneity is the most critical assumption made in thermocouple thermometry.*