Uncertainty analysis of Seebeck coefficient and electrical resistivity characterization

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1. Objective:

An uncertainty interval is required for the complete description of a material's thermoelectric power factor. The uncertainty may contain sources of measurement error including systematic bias error and precision statistical error. This work focuses specifically on the popular ZEM-3 (Ulvac Technologies) measurement system, but the methods apply to any measurement system. The analysis accounts for sources of systematic error including sample preparation tolerance, measurement probe placement, and thermocouple "cold-finger" effect; in addition to including statistical error.

2. Seebeck and Resistivity Measurement:

- Systems like the ZEM-3 measure Seebeck coefficient by a potentiometric (4-probe, see Fig. 1), differential method, using equilibrium or quasi-equilibrium measurements [1].
- Seebeck coefficient is calculated for a sample relative to the known Seebeck effect of the measurement probes.
- Stray interface voltages are accounted for by calculating Seebeck coefficient from the slope of a data set.
- Electrical resistivity is measured using a potentiometric (4-probe) arrangement, with electrical current passed through the sample in short pulses to avoid Peltier heating of the sample [2].
- A range of currents, often of different polarity, is used.

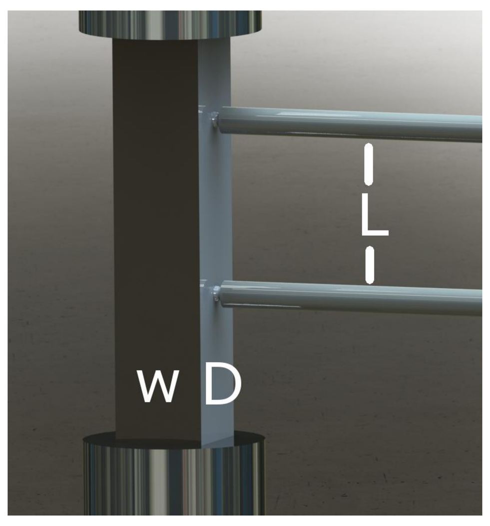


Fig. 1- Sample measurement configuration.

$$S = \frac{\Delta V}{\Delta T} - S_{Wire} = \frac{\sum x_i \sum y_i - N \sum x_i y_i}{(\sum x_i)^2 - N \sum {x_i}^2} - S_{Wire}(T)$$

$$\rho = \frac{\sum z_i \sum y_i - N \sum z_i y_i}{(\sum z_i)^2 - N \sum {z_i}^2} * \frac{w * D}{L}$$

$$x_i = Probe\ Temperature\ Difference\ [K]$$

$$y_i = Probe\ Voltage\ on\ Chromel\ Wires\ [V]$$

$$z_i = Sample\ Current\ [A]$$

See "Nomenclature" section

3. Sources of Uncertainty:

Resistivity Measurement

Source	Typical Values
Thermocouple Tip Radius	0.25 mm
Sample Uniformity*	±0.1 mm*
Thermocouple Separation Length	±0.1 mm
Caliper Resolution	0.01 mm
Statistical Variation†	Calculated†
DAQ Voltage Uncertainty	50ppm+1.2μV
DAQ Current Uncertainty	0.2%+0.3mA

*See Fig. 2 for examples
†See "Error Propagation" section

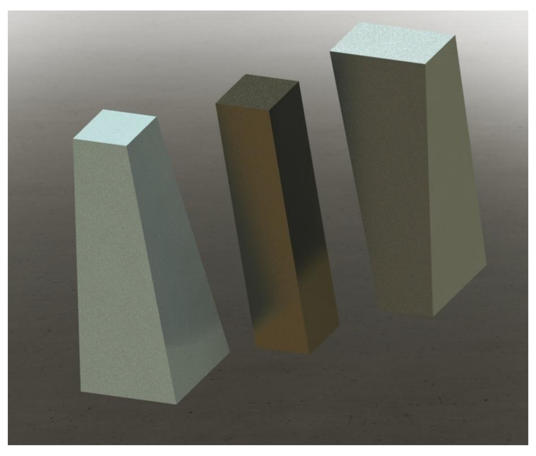


Fig. 2- Possible sample geometry uniformity issues.

Seebeck Measurement

Source	Typical Values
Cold-Finger Effect‡	Calculated‡
Wire Seebeck Variation	±3 %
Statistical Variation†	Calculated†
Absolute Temperature	±2 K
DAQ Voltage Uncertainty	50ppm+1.2μV
DAQ Temp. Uncertainty	50ppm+1.2μV

‡See "Cold-Finger Modeling" section
†See "Error Propagation" section

4. Error Propagation:

- Error propagation can be estimated from a Taylor series expansion (see Fig. 3) of the Seebeck and resistivity functions[3].
- Relative uncertainty "e" from a set of sources can be combined with a sum of squares method, as shown to the right. As an example the power factor uncertainty is calculated.
- Statistical uncertainty can be estimated for Seebeck and resistivity, a 95% C.I. is shown below.

$$U_{Statistical} = t_{\nu,95\%}\sqrt{\frac{N\sum(y_i - y_c(x_i))^2}{\nu(N\sum {x_i}^2 - (\sum x_i)^2)}}$$

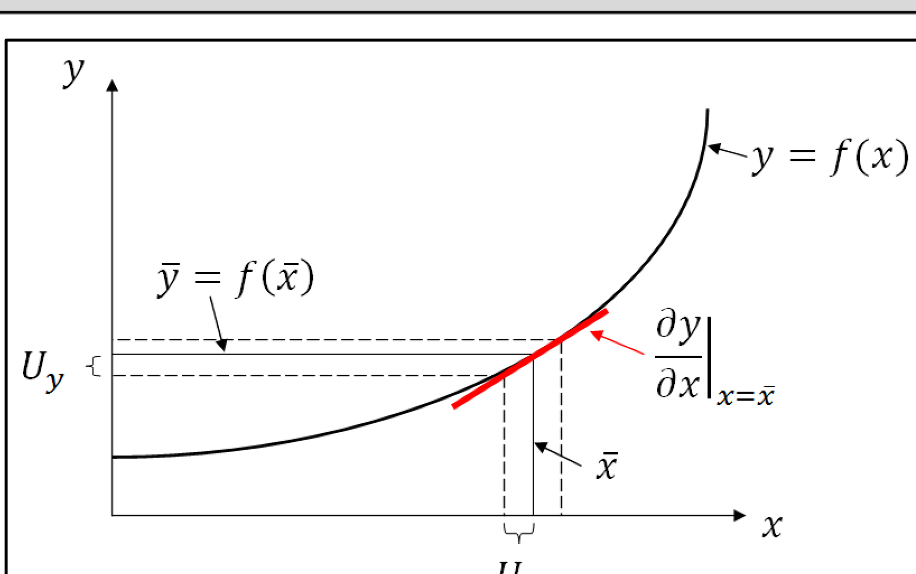


Fig. 3- Demonstration of error propagation.

$$\bar{y} \pm U_y = f(\bar{x} \pm U_x) \approx f(\bar{x}) \pm \left.\frac{\partial y}{\partial x}\right|_{x=\bar{x}} U_x$$

$$e_y = \frac{1}{\bar{y}}\left.\frac{\partial y}{\partial x}\right|_{x=\bar{x}} U_x$$

$$e_{Total} = \sqrt{{e_{y1}}^2 + {e_{y2}}^2 + \cdots}$$

$$U_{Power\ Factor} = \frac{\bar{S}^2}{\bar{\rho}}\sqrt{\left(\frac{2U_S}{\bar{S}}\right)^2 + \left(\frac{U_\rho}{\bar{\rho}}\right)^2}$$

See "Nomenclature" section

5. Cold-Finger Modeling:

- The cold-finger effect results when heat is conducted through a thermocouple. As a result the measured temperature is lower than the actual sample temperature.
- Since the effect is stronger in one probe than the other the Seebeck coefficient is overestimated.

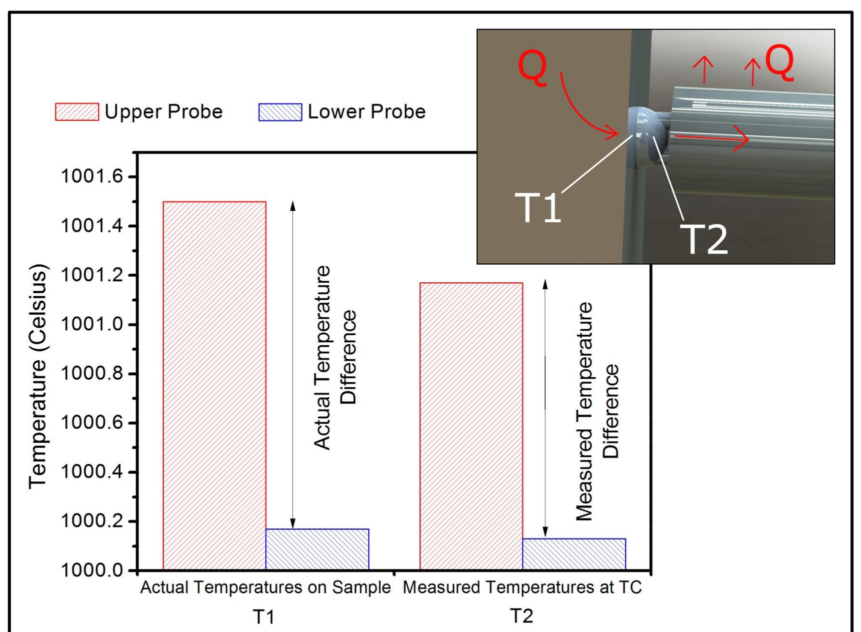


Fig. 4- Demonstration of cold-finger effect during a theoretical Seebeck measurement, using FEA.

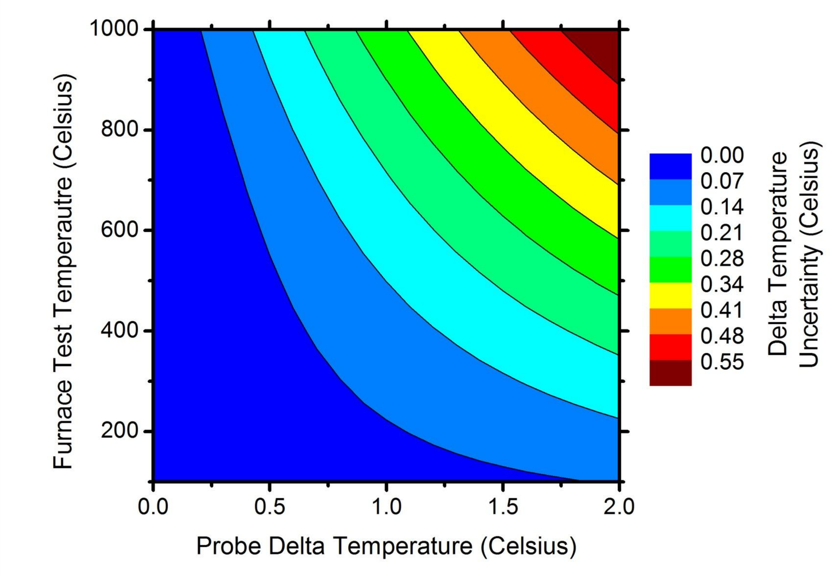
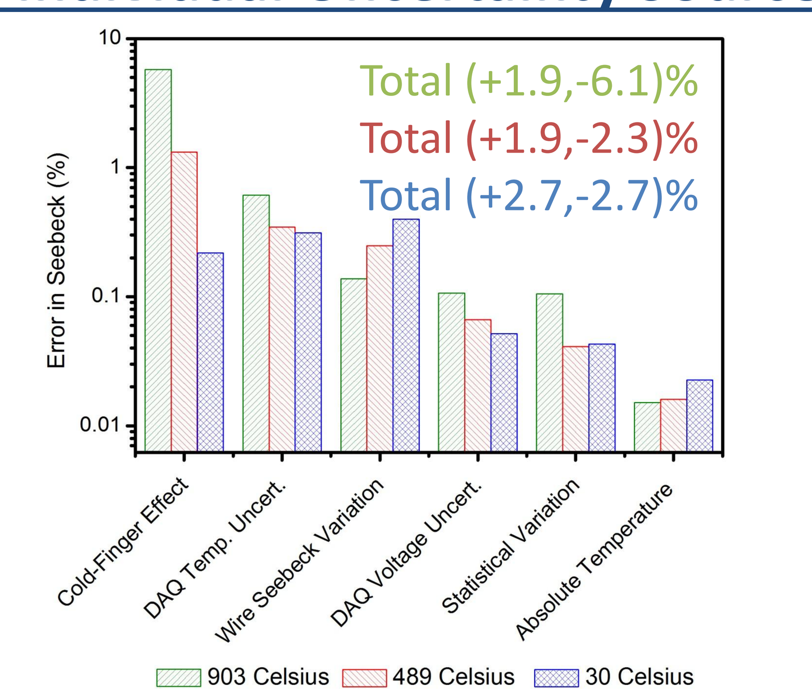
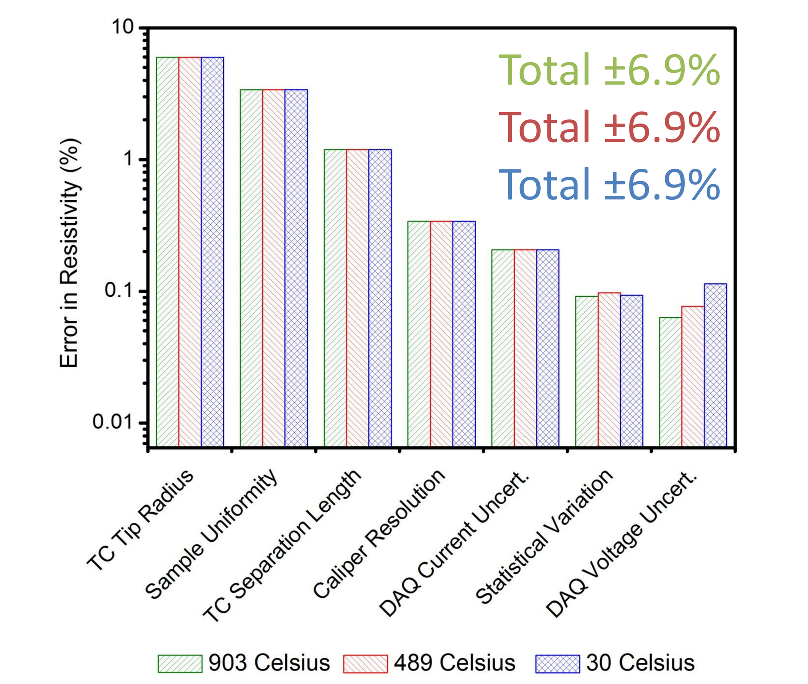


Fig. 5- Result of FEA study for a range of test delta temperatures and furnace temperatures.

- Thermal FEA shows the magnitude of the effect on the temperature differences (Fig. 5).
- The model (Fig. 1) was discretized using tetrahedral elements, a grid independence study demonstrated convergence.
- Sample ends were subject to fixed temperatures with all other faces subject to radiation, emissivity 0.7.

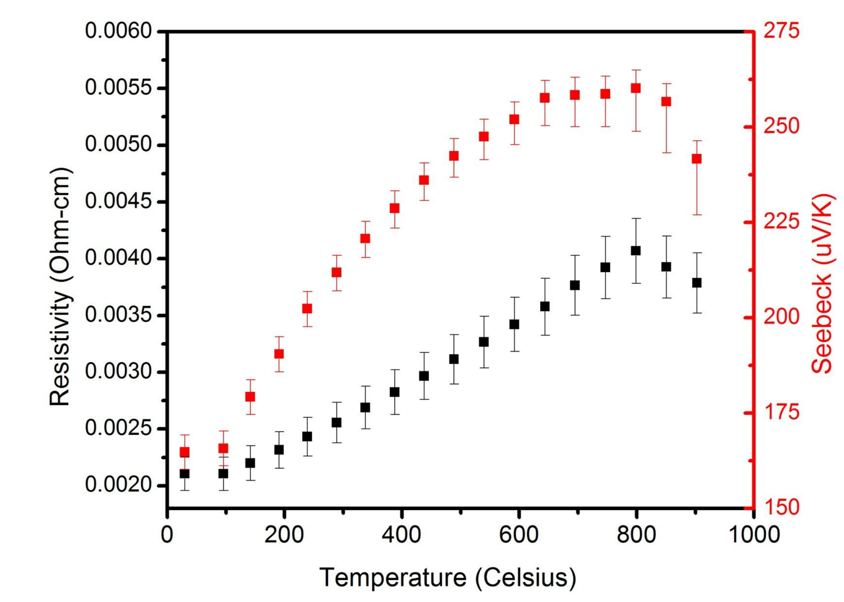
6. Individual Uncertainty Sources:

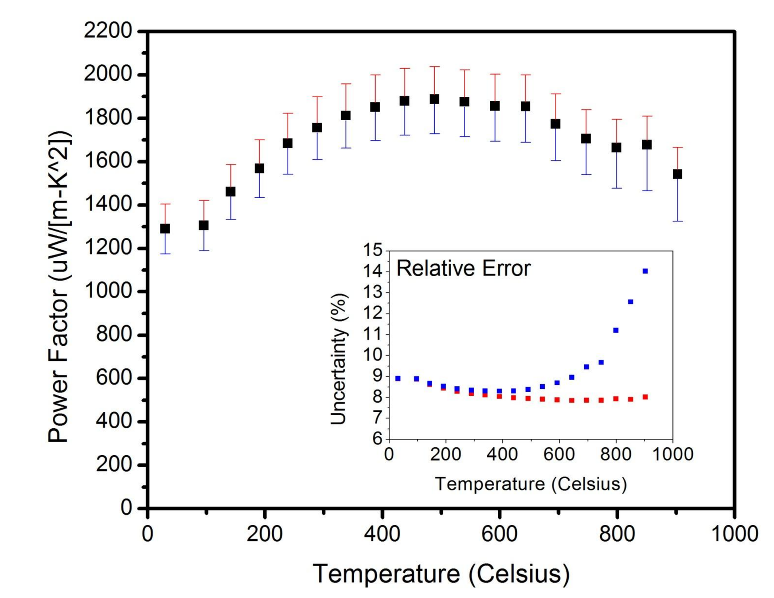




7. Cumulative Uncertainty Study:

Data shown for high temperature Si/Ge system, similar to NASA GPHS-RTG





8. Conclusion:

A conservative room temperature estimate of ±9% on power factor, and therefore minimum uncertainty on figure of merit, is calculated using a commercial measurement system. This room temperature error is dominated by the geometric errors involved in resistivity measurement. At higher temperatures the uncertainty is +9%/-15% due largely to the cold-finger effect on Seebeck measurements, this also impacts figure of merit. This uncertainty should be reported with all materials development.

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Nomenclature:

$S -$ Seebeck Coefficient	$L -$ Probe Separation Length	$\nu -$ Degrees of Freedom
$\rho -$ Electrical Resistivity	$D -$ Sample Depth	$t_{\nu,P} -$ Student's t-distribution
$T -$ Temperature	$w -$ Sample Width	$\bar{x} -$ Nominal Value
	$U_i -$ Uncertainty "i"	$N -$ Sample Size

References:

1. J. Martin, Meas. Sci. Tech. **8**, 24 (2013).
2. J. Martin, T. Tritt, and C. Uher, J. Appl. Phys. **12**, 108 (2010).
3. R.S. Figliola & D.E. Beasley, *Theory and Design of Mechanical Measurements, 5th Edition* (Wiley, 2010).