National Physical Laboratory

Good practice in TE materials metrology

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Objectives of this talk

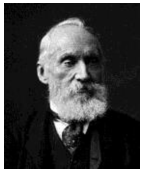
- Overview of **good practices** to measure **Seebeck coefficient, electrical conductivity and thermal conductivity**. The most common procedures and the associated typical sources of error are reviewed.
- What **uncertainty** values should we expect in measurements of **Seebeck coefficient, electrical conductivity or thermal conductivity**. But also when measuring **voltage/current, temperature or heat flux**.

What do we want to measure?

Thermoelectric effects:

Seebeck effect: transformation of heat into electric power. (responsible for electrical generation from wasted heat)

Peltier effect: transformation of electric power into heat in the junction of two different materials.



Thomson effect: absorption or emission of heat when a current is passing in the presence of a T gradient.

Peltier $\dot{Q} = (\Pi_A - \Pi_B) \cdot I$ $\Pi = S \cdot T$

Thomson $\dot{Q} = -\mu \cdot \Delta T \cdot I$ $\mu = T \cdot \frac{dS}{dT}$

What do we want to measure?

The ability of TE materials to generate electric power depends on three magnitudes:

S: generated voltage per ΔT degree. It should be high.

σ: how easily charged particles move. It should be high.

κ: how easily the heat is transferred. It should be low.

Seebeck coef.

Electrical conductivity

Figure of Merit, *zT*: $$zT = \frac{S^2 \cdot \sigma}{\kappa_L + \kappa_e} T$$

Thermal conductivity

Efficiency, *η*: $$\eta = \eta_C \cdot \frac{\sqrt{1 + Z\bar{T}} - 1}{\sqrt{1 + Z\bar{T}} + \frac{T_C}{T_H}}$$

Seebeck coefficient

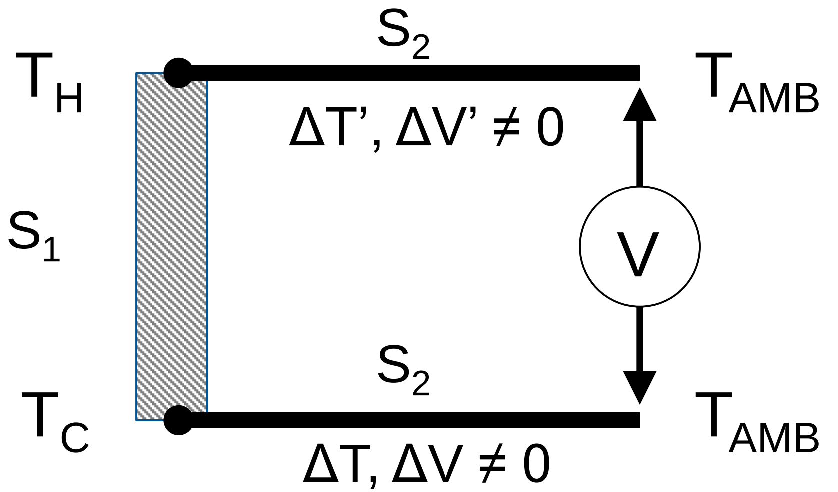
Generalities:

- The sample should be homogeneous
- It is usually given with respect to a reference material (measuring wire) that should be explicitly specified (or corrected).
- Seebeck coefficient Standard Reference Material: SRM 3451
  - Temperature range: 10 K – 390 K
  - Uncertainty ~ 3% @ 300 K (k=2)

!

$$S_{1,2} = -\frac{\Delta V}{\Delta T}$$

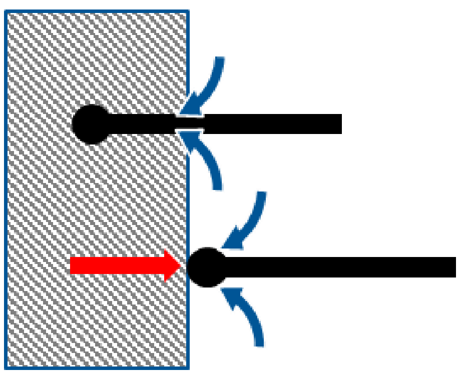
1 – Measured sample
2 – Reference material

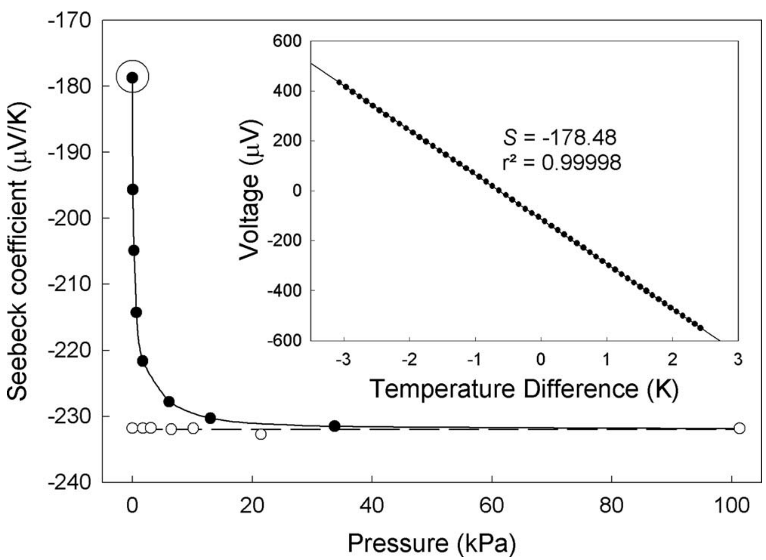


Seebeck coefficient

Mounting the temperature sensor

- (Bulk) ideally inserted in sample. Depth ~ 10 times diameter
- surface mounted: thermalize the tip. Vacuum might be worse.
- apply mechanical pressure or thermal contact material
- keep diameter of the sensor small to increase accuracy and minimise heat loss.





Mackey et al. Rev. Sci. Instrum. 85 (2014) 085119

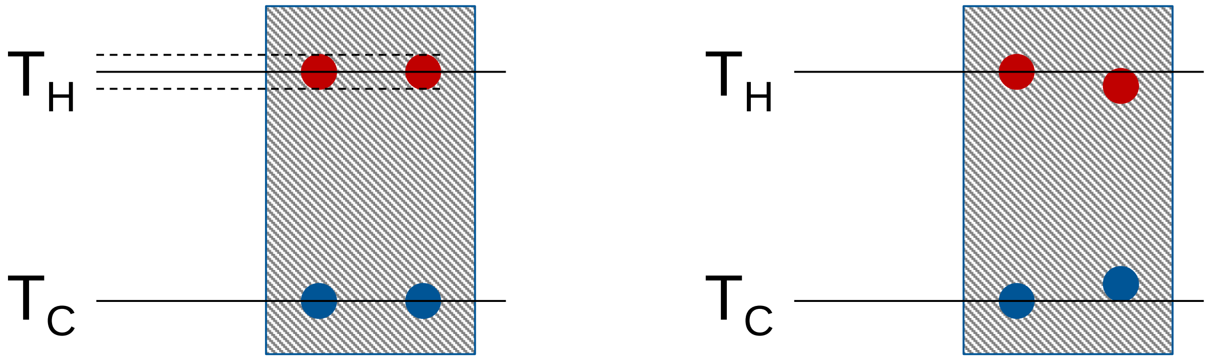
Seebeck coefficient

Two common set-ups: 2 or 4 probes.

4 probes: Seebeck and conductivity measurement

- T and V sensors must be located in the same isotherm in both sides.
- Different size of T and V sensors might give rise to different local heat dissipation
- T and V probes should be small

2 probe method is recommended.



Seebeck coefficient

Integral method:

- T_{cold} fixed
- Large ΔT
- Fitting model: “Difficult” to evaluate accuracy
- Closer to real conditions

$$S = -\left.\frac{dV}{dT_H}\right|_{T_C}$$

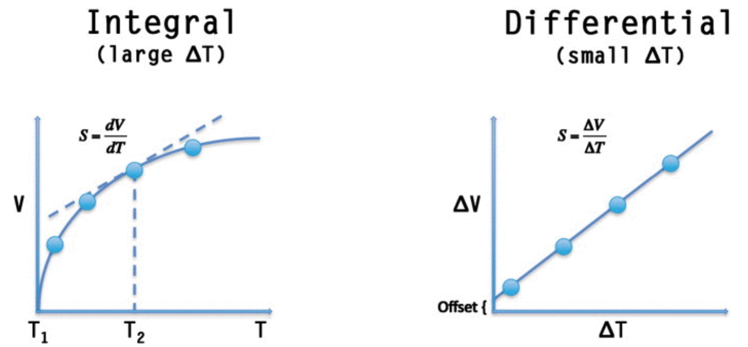
Differential method:

- The temperature control is simpler.
- Linear dependence small ΔT
- No influence from extraneous offset voltage.

$$S = -\frac{\Delta V}{\Delta T}$$

$\Delta T/T_{MEAN} << 1$

$\Delta S/S << 1$



J. Martin et al. Journal of Applied Physics, 108 (2010) 121101.

Seebeck coefficient

Uncertainty: what should we expect?

Cold finger effect:

- RT ~ 1-2 %
- HT (600 degC) ~ 8%

200 μV/K →

RT ~ 2 - 4 μV/K

HT (600 degC) ~ 16 μV/K

Measurement method:

- steady-state or quasi steady-state (qss)
- data acquisition sequential or simultaneous.

→ qss + sequential acquisition (2.3 s) → ~7% (15 μV/K)

Other variables difficult to quantify:

- Quality of thermal contact between sensor and sample
- Homogeneity of the sample
- State of the reference material (oxidation, contamination…)

Mackey et al. Rev. Sci. Instrum. 85 (2014) 085119

J. Martin, Rev. Sci. Instrum, 83 (2012) 065101

Electrical conductivity

Obtained from **resistance** and **physical dimensions**

Resistance:

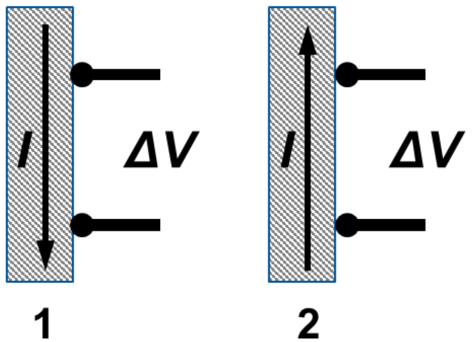
- Offset voltage (due to Seebeck effect)
- Peltier effect in contacts

Bipolar measurement
+ fast switching (AC bridge)

- Probe size

$$\boxed{\sigma = \frac{I \cdot L}{\Delta V \cdot A}}$$

$$\Delta V_1 = IR + S\Delta T$$
$$\Delta V_2 = IR - S\Delta T$$



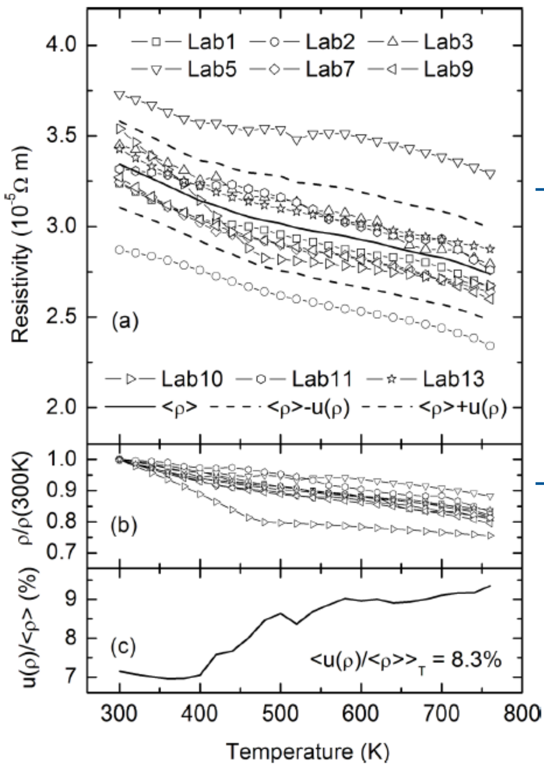
- Contact resistance (~1 – 10³ μΩ·cm²)
- Wire resistance (1 – 10 mΩ)

4-probe method

Electrical conductivity

Physical dimensions

One of the most common sources of error, and one of the least intuitive

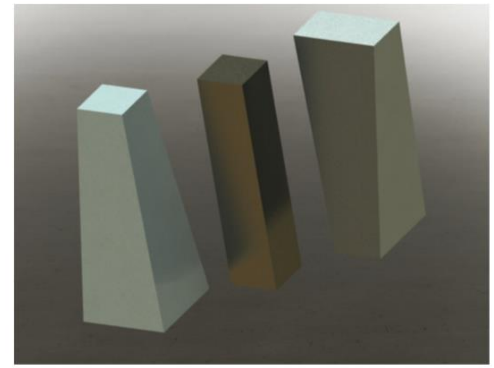


$$\rightarrow \left\langle \frac{u(\rho)_{geo}}{\langle\rho\rangle} \right\rangle_T = 7.3\%$$

$$\rightarrow \left\langle \frac{u(\rho)_{ideal}}{\langle\rho\rangle} \right\rangle_T = 3.7\%$$

E. Alleno et al. Rev. Sci. Instrum. 86 (2015) 011301

SAMPLE PREPARATION



Mackey et al. Rev. Sci. Inst. 85 (2014) 085119

MEASUREMENT OF DIMENSIONS

No. 40 *Callipers and micrometers*

No. 80 *Fundamental good practice in dimensional metrology*

http://www.npl.co.uk/publications/guides/

Electrical conductivity

Other methods: van der Pauw.

Strong requisites:

- thin film technique (although with adequate sample preparation can be used for bulk as well).
- homogeneous material
- continuous (no voids)

Good practices

- Position of the probes depends on the geometry of the sample
- Bipolar measurements are recommended
- Metallisation to improve contact
- Current intensity low to avoid heating by Joule effect $\begin{cases} \text{semic.} \sim \mu A \\ \text{metal} \sim mA \end{cases}$

Electrical conductivity

Uncertainty: what should we expect?

Resistance:

- Calibrated instrument
- Polarity inversion
- Fast switching (AC bridge)
- 4-probe resistance method
- Probe size

~ 2-3 %

up to ~ 6%*

Physical dimensions:

- Sample preparation
- Sample section
- Distance between probes

~ 3-4 %

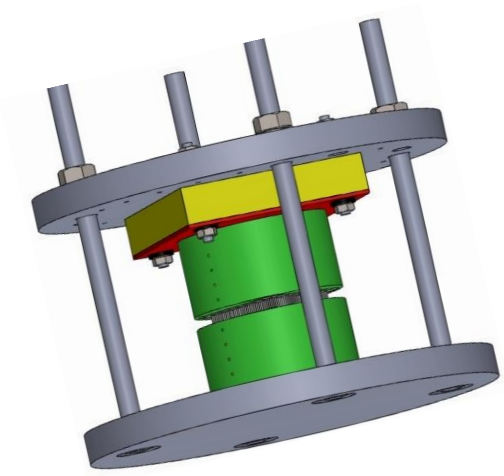
*Mackey et al. Rev. Sci. Instrum. 85 (2014) 085119

Thermal conductivity

→ 12:15 Ekaterina's talk: "Heat flux measurements"

Key aspects:

- Accurate measurement of the heat flux through the sample
  - Accurate measurement of the temperature
  - Control over the heat losses
- Minimise and quantify the (unavoidable) thermal contact resistance



Thermal conductivity

Accurate measurement of temperature

- Choice of temperature sensor

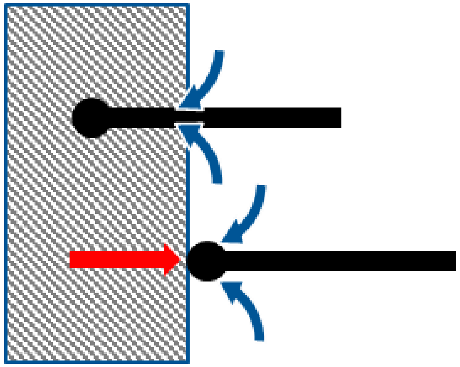
Criteria	Thermocouple	RTD	Thermistor
Temp Range	-267°C to 2316°C	-240°C to 649°C	-100°C to 500°C
Accuracy	Good	Best	Good
Linearity	Better	Best	Good
Sensitivity	Good	Better	Best
Cost	Best	Good	Better

Typical uncertainties

Thermocouples:
type-K: **2 ºC or 0.75%**
type-R/S: **0.15 ºC** @ 962 ºC
up to 2 ºC @ 1450 ºC

PT-100:
Class A= ±**(0.15 + 0.002*t) ºC**
or 100.00 ±0.06 Ω @ 0ºC
Class B = ±**(0.3 + 0.005*t)** ºC
or 100.00 ±0.12 Ω @ 0ºC

- Mounting the temperature sensor



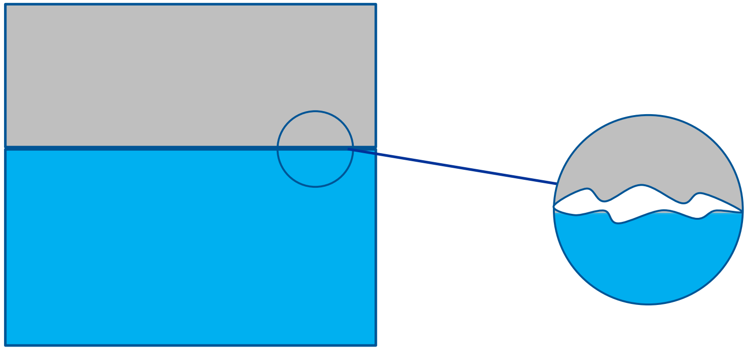
- ideally inserted in sample. Depth~10· diameter
- Good thermal contact with sample (mechanical pressure/ thermal contact material)

http://digital.ni.com/public.nsf/allkb/C50FA55B3B2F85D9862572D00083350E
http://www.omega.com/prodinfo/Integrated-Circuit-Sensors.html

Thermal conductivity

The thermal contact resistance cannot be avoided but it can be minimised:

- Preparing adequately the sample. Polish it to reduce roughness and improve flatness and parallelism.
- Prepare adequately the hot and cold plates in contact with the sample
- Avoid large thermal gradients in the sample (thermal expansion)
- Use thermal interface material: thermal paste, graphite paper.
- Apply mechanical pressure.



Thermal conductivity

Indirect methods: thermal diffusivity.

$$\kappa = \alpha \cdot C_p \cdot \rho$$

- Addition of the uncertainties of the heat capacity (C_p) and the density (ρ) (the latter including the physical dimensions as well)
- Transient methods for thin films and nanostructures (LFA, Photo-acoustic…) usually they rely on mathematical models where the input of 5 or 6 variables is needed.
- Difficult to include thermal contact resistance.
- Difficult to estimate the uncertainty associated.
- Validation with standard reference material (BCR-724)

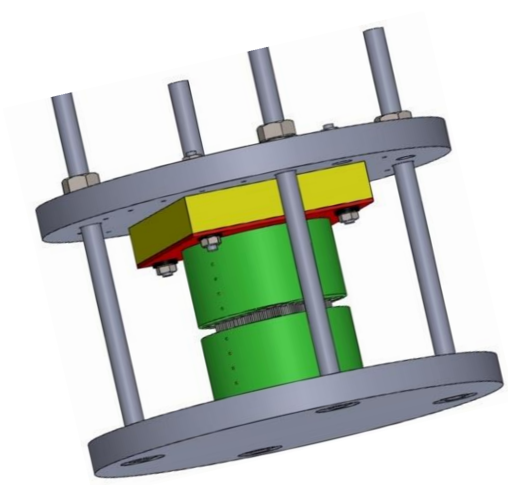
Thermal conductivity

Uncertainty: what should we expect?

Depends strongly on the method

Uncertainty of the Standard Reference Material BCR-724 ~ 6% (k=2)

→ 12:15 Ekaterina’s talk: “Heat flux measurements”



zT measurements

Combination of Seebeck coefficient, electrical conductivity and thermal conductivity (and the temperature).

$$zT = \frac{S^2 \cdot \sigma}{\kappa_L + \kappa_e} T$$

Some examples:

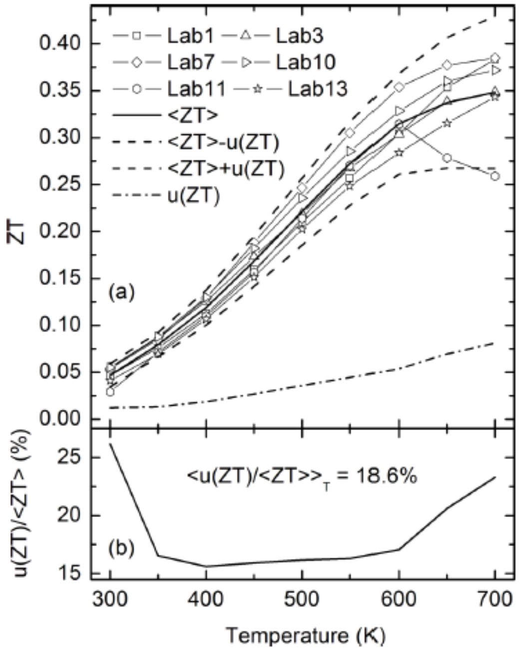
- S ~ 5%
- σ ~ 7%
- κ ~ 7%

→ zT ~ 14%

- S ~ 8%
- σ ~ 9%
- κ ~ 10%

→ zT ~ 21%

zT measurements



$Co_{0.97}Ni_{0.03}Sb_3$ round robin (2015)

France (7), Switzerland (1), Czech Republic (1)

zT ~ 16% – 25%

zT ~ 12% – 21%

Bi_2Te_3 round robin (2013)

USA (5), Germany (1), China (1), Canada (3)

Table I. Round-robin uncertainties based on data scatter (maximum scatter from the mean value divided by the mean value)

T (K)	δ_D	δ_{Cp}	δ_α	δ_k	δ_{PF}	δ_T	δ_{ZT}
300	0.004	0.050	0.172	0.092	0.071	0.010	0.117
325	0.004	0.050	0.144	0.108	0.117	0.010	0.159
350	0.004	0.050	0.142	0.085	0.088	0.010	0.122
375	0.004	0.050	0.117	0.108	0.111	0.010	0.155
400	0.004	0.050	0.096	0.128	0.093	0.010	0.158
425	0.004	0.050	0.068	0.151	0.077	0.010	0.170
450	0.004	0.050	0.095	0.153	0.080	0.010	0.173
475	0.004	0.050	0.078	0.179	0.108	0.010	0.209

The uncertainties for density, C_p, and temperature are assumed to be constant over the temperature range.

E. Alleno et al. Rev. Sci. Instrum. 86 (2015) 011301

H. Wang et al. J. Electronic Materials, 42 (2013) 1073-1084

Conclusions

National Physical Laboratory

- Overview of good practices to measure Seebeck coefficient, electrical conductivity and thermal conductivity.
- The most common procedures and the associated typical sources of error have been reviewed.
- Typical uncertainty values associated to Seebeck coefficient, electrical conductivity and thermal conductivity.

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