Uncertainties in thermoelectric materials

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Message of today

1. **Every measurement is subject to some uncertainty**
    - There is an internationally agreed way to quantify this uncertainty

"Any inference from the particular to the general must be attended with some degree of uncertainty, but this is not the same as to admit that such inference cannot be absolutely rigorous, for the nature and degree of the uncertainty may itself be capable of rigorous expression."

R. A. Fisher (1966)

What is NPL
What are we doing

NPL: The UK’s national standards laboratory

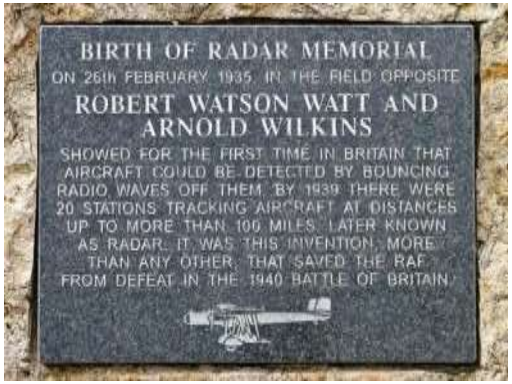
- **For more than a century NPL has developed and maintained the nation's primary measurement standards.** Founded in **1900**
- Over 500 scientists, based in south-west London.
- 36,000 square-metre purpose built measurement building with 388 of the world's most extensive and sophisticated

What we do

- Develop & disseminate UK’s measurement standards, ensure they are internationally accepted
- Multidisciplinary R&D and technical services for public and private sector

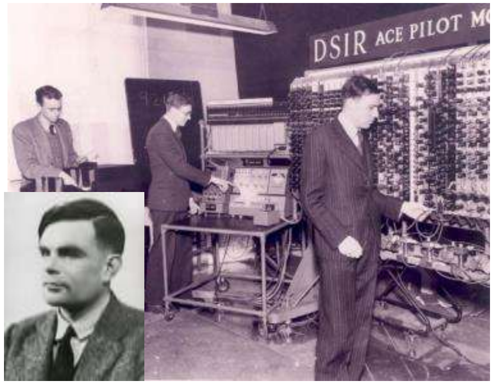
A long history …

NPL
National Physical Laboratory

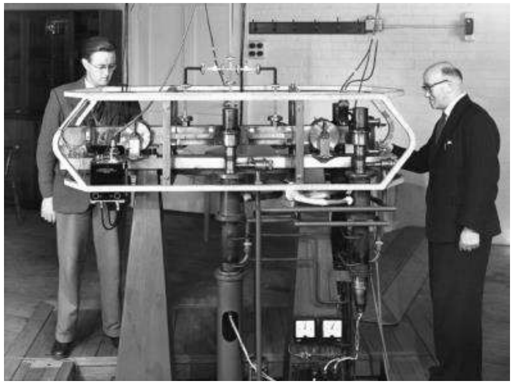


BIRTH OF RADAR MEMORIAL
ON 26th FEBRUARY 1935 IN THE FIELD OPPOSITE
ROBERT WATSON WATT AND
ARNOLD WILKINS
SHOWED FOR THE FIRST TIME IN BRITAIN THAT AIRCRAFT COULD BE DETECTED BY BOUNCING RADIO WAVES OFF THEM. BY 1939 THERE WERE 20 STATIONS TRACKING AIRCRAFT AT DISTANCES UP TO MORE THAN 100 MILES. LATER KNOWN AS RADAR, IT WAS THIS INVENTION, MORE THAN ANY OTHER, THAT SAVED THE RAF FROM DEFEAT IN THE 1940 BATTLE OF BRITAIN.

The invention of Radar 1935



Turing and World's first Automatic Computing Engine (ACE) 1946



World's first Caesium Atomic Clock 1955

Packet-switching developed at NPL 1966

Weighing Concorde 1980

Fixing Big Ben 1976

NPL Thermoelectric activity

Our mission,

as defined by our **industrial advisory group**,

is to measure thermal and electrical semiconductor materials properties at a scale below 1 micrometre with enough **accuracy**

to allow the rapid adoption of emerging materials into

more efficient commercial devices

- £/watt
- Manufacturing Readiness Level
- Designing with uncertainty
- Thermal and electrical transport in heterogeneous materials

NEXTEC

Nextec

Nanostructured thermoelectric skutterudite

Skutterudite is a cobalt arsenide mineral with a cage structure that has variable amounts of nickel and iron substituting for cobalt with a general formula: (Co,Ni,Fe)As_3.

- Ambitious and wide ranging objectives covering;
  - Thermoelectric nanomaterials development
  - Development of novel metrology tools
    - 3D Van der Pauw Method
    - Improved “On-Top” 3omega microchips; “Pressed onto” ZTMeter
    - Thin-film TE measurement
    - Microwave cavity measurement
  - Pioneering in module development
    - Pioneering Ring module for cars
    - Planar energy generation modules
    - Planar cooling modules
  - Life cycle impact analysis of nano TE materials

Electrolux

SIEMENS

Fraunhofer
IPM

CSIC

KTH
VETENSKAP OCH KONST
KTH Information and Communication Technology

LEITAT
managing your technologies
Technological Center
member of TECNIO

EL ARTE DE REFRIGERAR
TERMOELECTRICIDAD
CIDETE
INGENIEROS

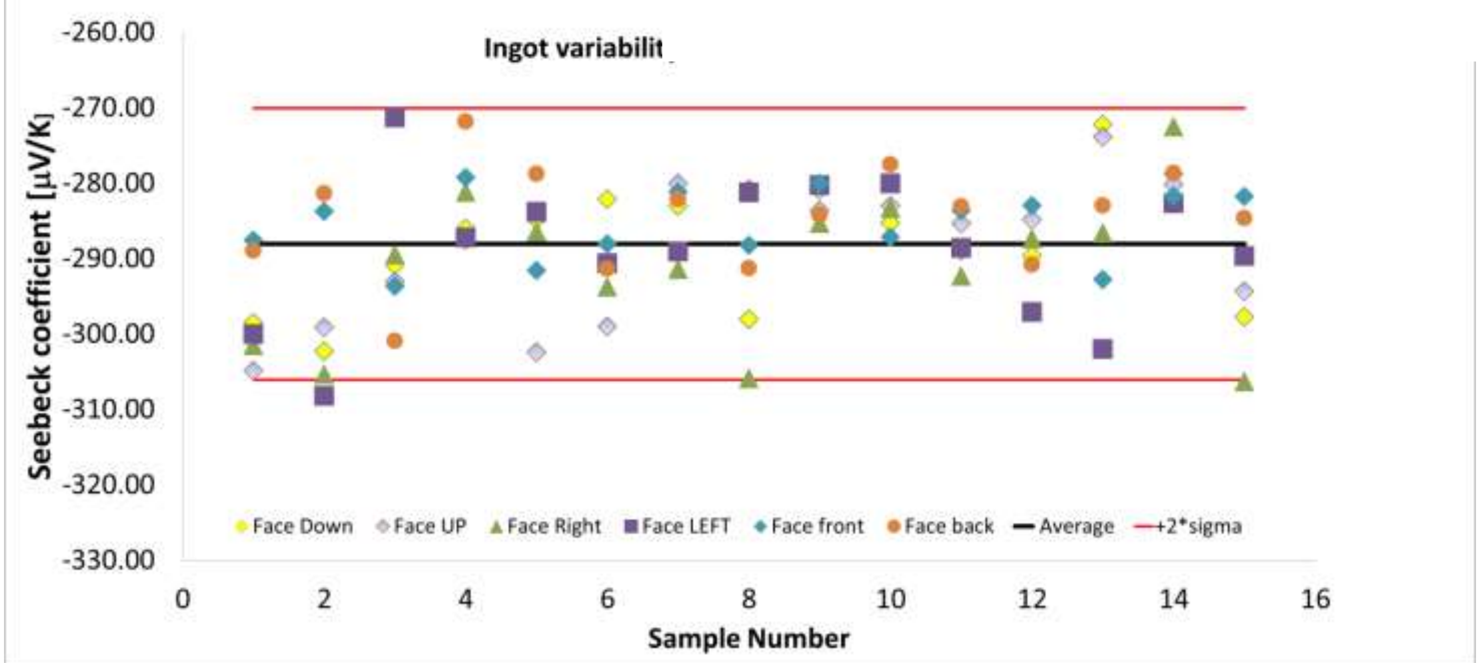
SEAT

Materials uniformity and anisotropy

Large scale production requires properties to be kept constant across ingot – similar to doping uniformity in wafer processing

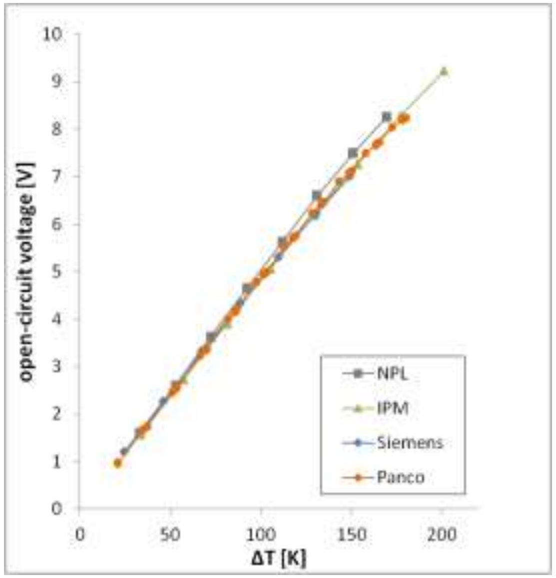
Disc-shaped compacted $CoSb_3$-Skutterudite (CSIC-SPS 641) cut in 15 cubes. The size of the cubes is for this example 2x2x2 mm^3

All results are within the 95% confidence interval (coverage factor k=2)

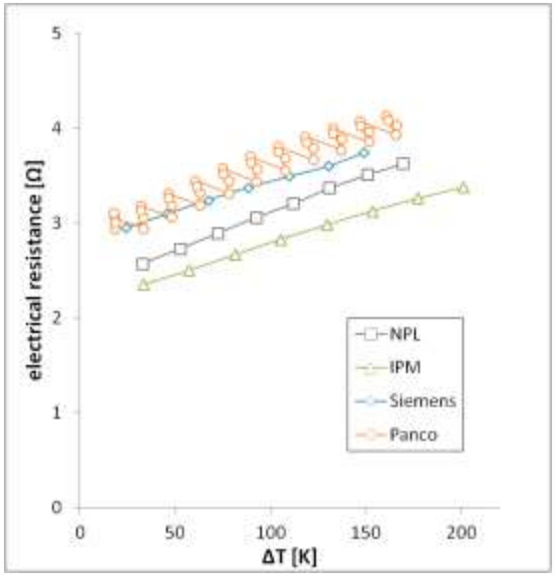


Comparison with Siemens- Panco and Fraunhofer

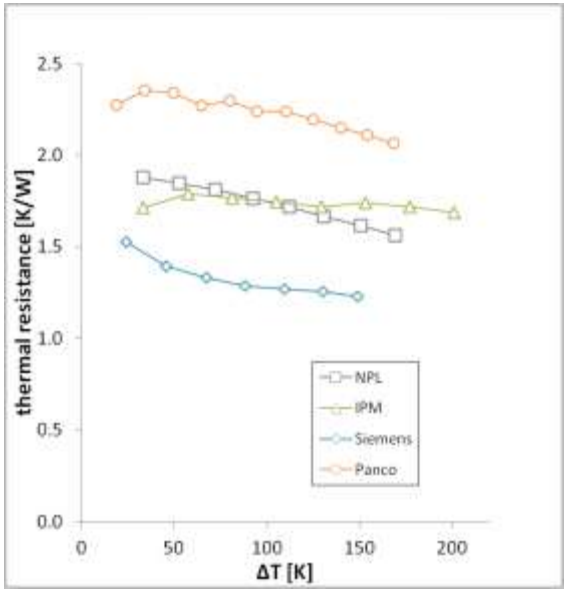
Open-circuit voltage



Internal electrical resistance



Thermal resistance



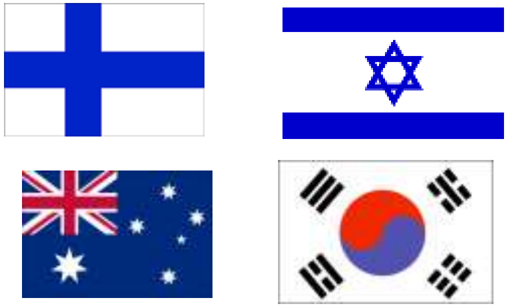
- Open-circuit voltage: Good agreement
- Internal electrical resistance: Unexpected scatter
- Thermal resistance: Expected scatter

Both T hot and T cold are key to comparison

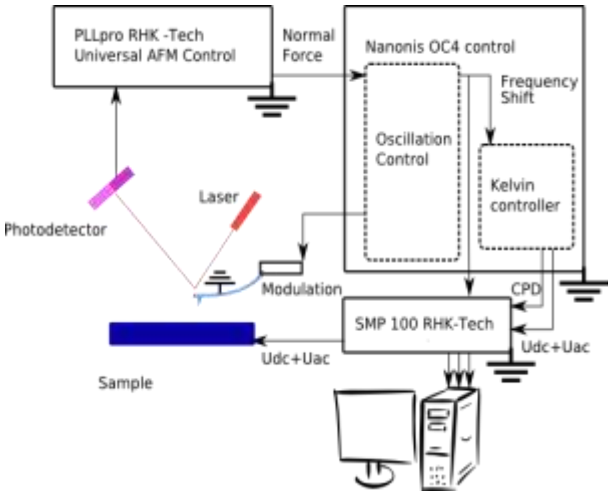
Current Annex VIII Participants

- **IEA-AMT Thermoelectric Annex**
  - Annex lead: Oak Ridge National Laboratory (H. Wang)
  - USA: GMZ (G. Joshi); Clemson (T. Tritt); Marlow (J. Sharp); GM R&D (J. Salvador); Army Research Laboratory (P. Taylor)
  - China: SICCAS (S.Q. Bai, L. Chen)
  - Canada: CANMET(Y.C. Tseng); University of Waterloo (H. Kleinke);
  - Germany: Fraunhofer IPM (J. König)
  - United Kingdom: NPL (A. Cuenat)

- **IEA-AMT members countries:**
  - Finland: VTT
  - Israel:
  - Australia:
  - Korea: KERI (H. W. Lee)



Nanoscale traceability of thermoelectric measurements



1) Current
2) EM force
3) Kelvin probe – Work function

5) Thermistor
4) RF oscillation (~1 GHz)

Accuracy + models required:

- feedback loop
- probe convolution
- nanoscale transport …

“Quantitative nanoscale surface voltage measurement on organic semiconductor blends”
Cuenat et al, Nanotechnology 23 045703 (2012)

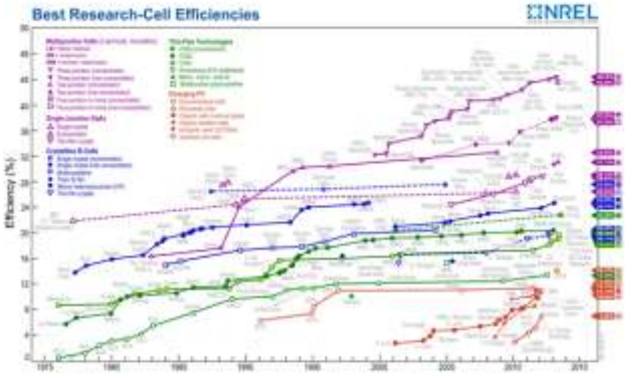
Main problem for AFM is to be **quantitative rather than qualitative**

Metrology for manufacturing 3D integrated circuits
3D Stack

WP1	WP2	WP3
TSV	**Bonding/Thinning/microbump**	**Conformity assessment Standardization**
AFM and SEM-FIB standards for the traceability of dimensional measurement	IR microscopy and laser scanning IR for post bonding overlay alignment towards very high overlay uncertainty requirement of 0.1 µm for microns size TSVs	Improve draft Standards SEMI 5506 and 5616: curvature, surface roughness and flatness at die level coupled with wafer level information. Post-bond overlay alignment.
Reference free synchrotron radiation based methods for LBS layers measurements	Standard 3D areal measurement parameters at the different scale (interconnect, die, wafer) and traceability to metrological AFM.	Application of GUM for Conformity assessment to electrical and thermal properties, critical dimension parameters for TSV and wafer alignment.
SPM methods for 3D nanoscale electrical and thermal transport properties of Cu filled HAR TSV	Characterize contamination, interface defectivity and adhesion, stress relaxation and thermal dissipation at surface and interface of bonded/thinned wafers/dies	Good practice guides to traceable measurement for 3D HAR TSVs
SMM and GHz SAM technique as on wafer metrology tool to characterize submicron voids	Wafer level bump inspection (height, width, defects) based on triangulation and image correlation	
On wafer RF measurements of electrical parameters of high density TSVs		

European Metrology Project Energy 51: Metrology for III-V materials based high efficiency multi junction solar cells

http://projects.npl.co.uk/solcell/



44% efficiency, no need for cooling

New media transfer
- Dedicated website
- Biannual E-Newsletter
- 4 E-training modules

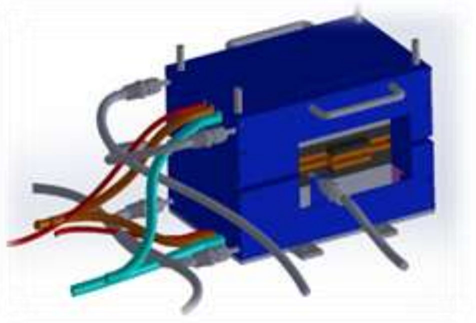
Standards and calibrations
- 4 Best practice guides
- At least 2 Technical standard reports to IEC and ISO
- 9 New NMI Measurement services

Training and dissemination
- 2 Training workshops
- 2 Special conference sessions.
- 14 peer-review publications

Stakeholder engagement
- Biannual stakeholder meeting
- 3 Trade magazine articles
- 12 Reports and white papers
- LETI annual review (> 320 people from 120 companies)

Modules metrology

At NPL, we are developing facilities to measure **traceably** the performance of thermoelectric generators (TEG)



“**Traceability**: the result can be related to a reference through a documented unbroken chain of **calibrations,** each contributing to the **measurement uncertainty**”

- **Precision: reproducibility**
- **Accuracy: “true value”**

Low accuracy
High precision

Higher accuracy
Low precision

High accuracy
High precision

Tomorrow’s presentation: Better than 0.1% power repeatability

Short review of uncertainties in thermoelectric materials measurement

Tomorrow : modules!

Why is metrology important

Who needs it

- Industry

- Science

- Doctors

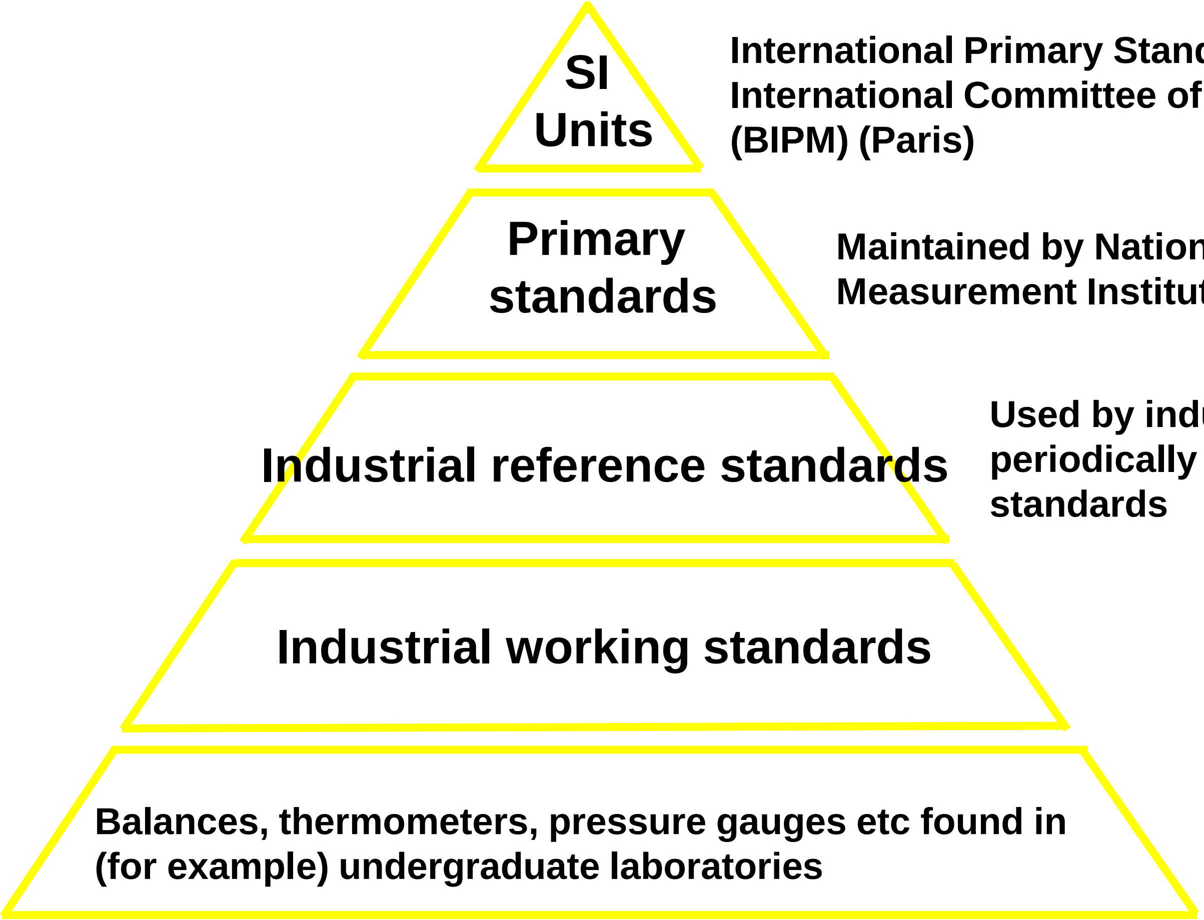
- Regulators

- You and I

Why is it needed

- Accurate, consistent measurement enables fair trade
- It guarantees manufacturing quality and supports innovation
- It underpins our safety, our health and our quality of life
- It facilitates environmental management
- It provides for effective regulation
- Allows to rigorously test and evaluate new and established scientific theories.

Standards are traceable through a chain of comparisons



SI Units

International Primary Standards, set by International Committee of Weights and Measures (BIPM) (Paris)

Primary standards

Maintained by National Measurement Institutes

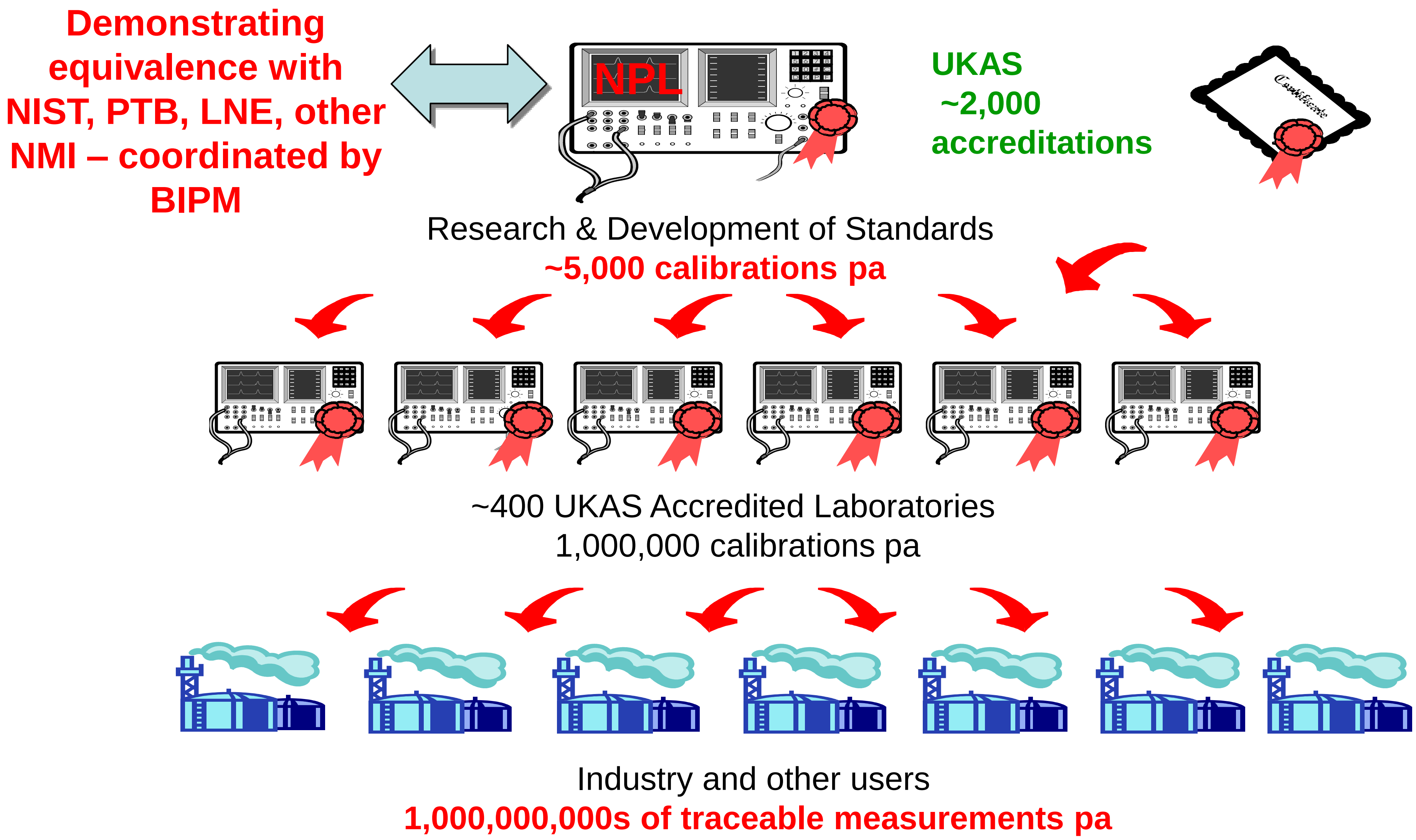
Industrial reference standards

Used by industry and checked periodically against Primary standards

Industrial working standards

Balances, thermometers, pressure gauges etc found in (for example) undergraduate laboratories

NPL at the heart of the UK Measurement infrastructure



Demonstrating equivalence with NIST, PTB, LNE, other NMI – coordinated by BIPM

UKAS
~2,000
accreditations

Research & Development of Standards
~5,000 calibrations pa

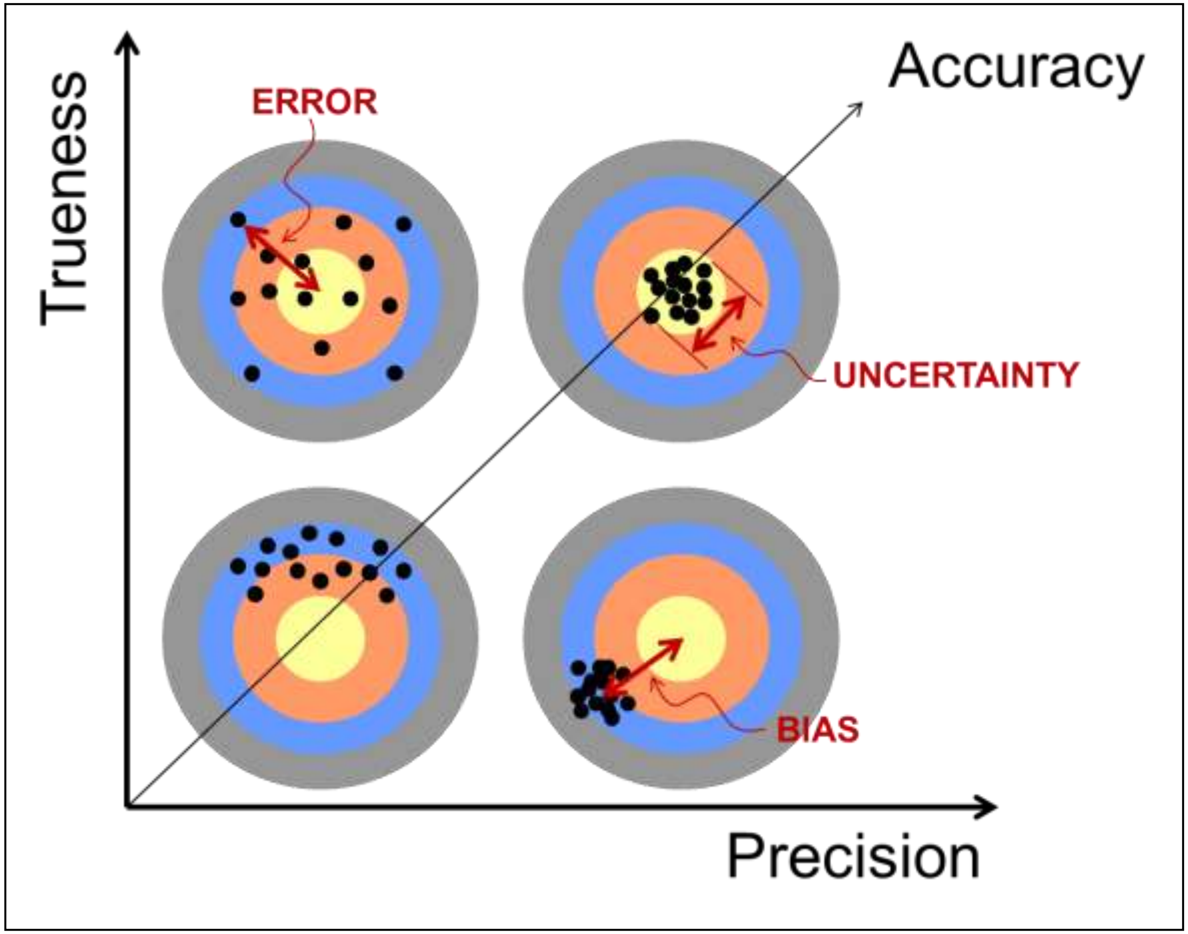
~400 UKAS Accredited Laboratories
1,000,000 calibrations pa

Industry and other users
1,000,000,000s of traceable measurements pa

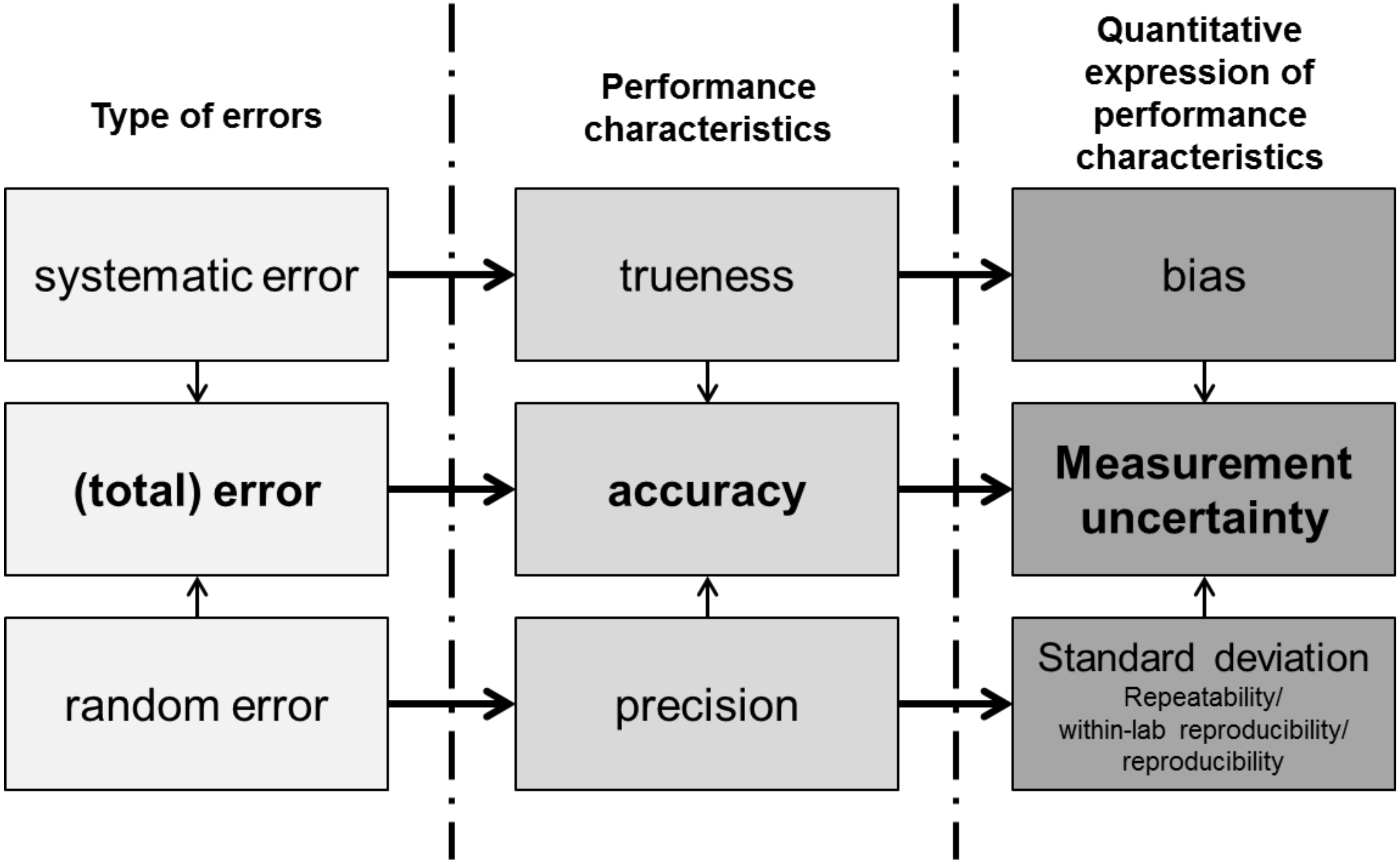
Why do we need uncertainties

- To meet specifications
  - to “operate within the uncertainty budget”
  - to know the most important (largest) uncertainties –and to reduce them
- To manage risk
- To improve – by knowing or reducing measurement uncertainty:
  - to increase quality, efficiency, utilisation
  - to reduce energy, waste, re-work

Precision, accuracy and trueness



Error and uncertainty



Adapted from “Understanding the meaning of accuracy, trueness and precision”. A. Menditto et al. *Accred. Qual. Assur.* **12** (2007) 45 - 47

Seebeck coefficient

International round robins (interlaboratory reproducibility!):

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

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

u_S (T ~ 300K) → ±~10%

u_S (350K < T < 600K) → ±~5%

u_S (T ~ 700K) → ±~10%

→

$\boxed{\bar{u}_S \rightarrow \pm 6\%}$

Conf. level = 68%

Bi_2Te_3 round robin (2013)

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

“scatter about” $\boxed{\pm 5.5\% \ (\pm 4\% \text{ for ZEM-3 users})}$

Seebeck coefficient

Instrument and the measurement protocol uncertainty

- Simultaneous acquisition of T and V → **differences up to 9%**
- Thermal contact:
  - Gas pressure → **differences up to 6%**
  - Contact geometry → **differences up to 14%**
- Thermal stability
- Type of Thermocouple
- Type of multimeter (T and V acquisition)
- Temperature of the reference junction

J. Martin, "Protocols for the high temperature measurement of the Seebeck coefficient in thermoelectric materials." Rev. Sci. Inst. 2012, 83, 065101.

What can we get (if all the previous points are taken into account)?:

ZEM-3:
- ±1% @ RT
- +1% / -13% @ High T (Cold finger effect)

J. Mackey, F. Dynys, A. Sehirlioglu. "Uncertainty analysis for common Seebeck and electrical resistivity measurement systems." Rev. Sci. Inst. 2014, 85(8), 085119.

NIST: ±"2.1% " PTB: ±"2.9% "

J. Martin, "Apparatus for high temperature measurement of the Seebeck coefficient in thermoelectric materials." Rev. Sci. Inst. 2012, 83, 065101.

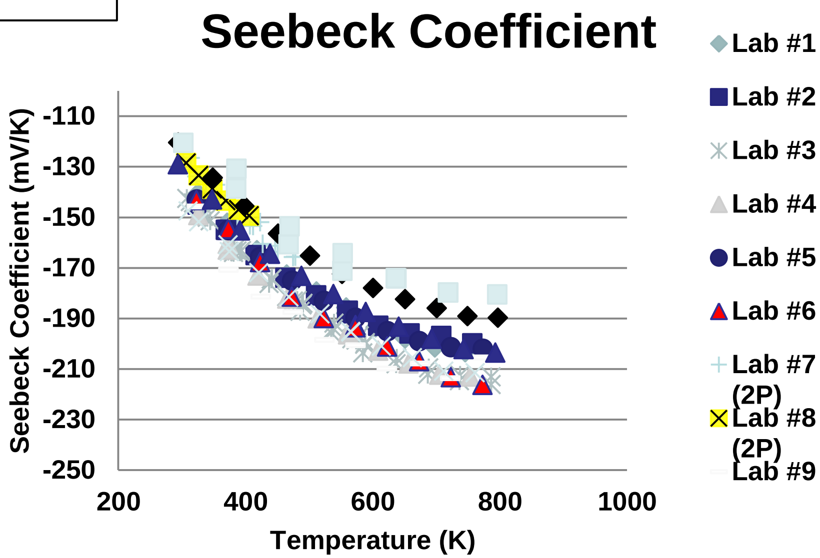
Seebeck coefficient

Therefore:

- Reproducibility (Round robins) : ~6%
- Instrumental: ~ +1/-13%

Combined Uncertainty ~ +6/-14.3%

(68% conf. level)



IEA results:
Electrical resistivity for n-type half-Heusler

Electrical resistivity/resistance

International round robins (only reproducibility!):

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

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

u_ρ (300 K < T < 400K) → ±~7%

u_ρ (500 K < T < 750K) → ±~9%

➔ $\boxed{\bar{u}_S \rightarrow \pm 7.3\%}$

Conf. level = 68%

Normalised resistivity
(no geometrical factor)

$$\frac{\rho\ (T)}{\rho\ (300\ K)} = \frac{R(T)}{R(300K)}$$

➔ $\boxed{\bar{u}_S \rightarrow \pm 3.7\%}$

Conf. level = 68%

Bi_2Te_3 round robin (2013)

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

“scatter about” $\boxed{\pm 12.5\%}$

Electrical resistivity/resistance

Resistivity:

Geometrical factors:

- Distance between probes
- Probe size
- Section of the sample
- Calliper/Micrometer resolution

Most important factor!

Voltage factors:

- Multimeter(s) accuracy
- Offset drift

Statistical factors:

- Repeatability
- Reproducibility

Some numbers: ZEM-3: ±7% ∀T

J. Mackey, F. Dynys, A. Sehirlioglu. “Uncertainty analysis for common Seebeck and electrical resistivity measurement systems.” Rev. Sci. Inst. 2014, 85(8), 085119.

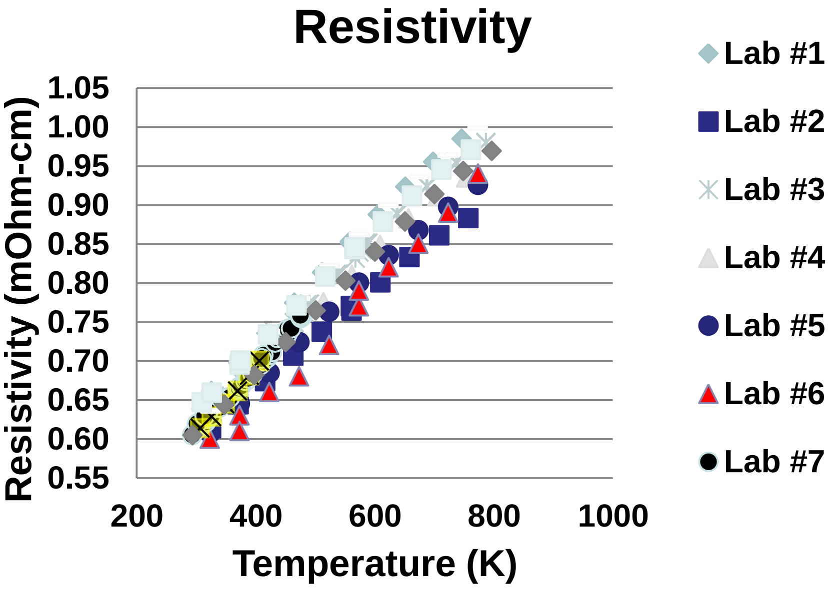
Electrical resistivity/resistance

Therefore:

- Reproducibility (Round robins) : ~ 7.3%
- Instrumental: ~ 7%

Combined Uncertainty ~ 10%

(68% conf. level)



IEA results:
Electrical resistivity for n-type half-Heusler

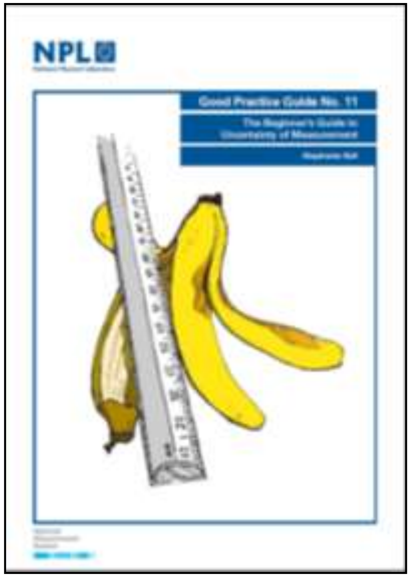
Electrical resistivity/resistance

If the main factor is measuring the dimensions of the sample…

How should we measure geometrical dimensions?

No. 11

The beginners guide to uncertainty of measurements



No. 40

Callipers and micrometers

No. 80

Fundamental good practice in dimensional metrology

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

Thermal conductivity

Absolute method:

- └→ **No** reference sample
- └→ Heat flux = I·V ➔ Guarded methods!

NPL Guarded hot plate: ±2% @ RT; ±5% @ HT

(ASMT-C177; ISO 8302)

Non-absolute methods:

- └→ **Need** reference sample

- Thin heater: ±3%
- Heat flow meter: ±2%
- Guarded comparative longitudinal: ±5%

\+ ≳ 4% reference sample!

Thermal conductivity

Thermal diffusivity, Cp and density

- Laser flash: ~2%
- Heat capacity: ~1%
- Density: $\lesssim 1\%$

Absolute best case scenario

Sample requirements and data corrections needed:

- Homogeneous of the sample
- Correction for thermal expansion
- Flat sample
- Parallel faces
- Squareness of the sample
- Constant density in the T range

Only geometrical can be +5%

Thermal conductivity

Round robins (reproducibility):

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

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

$\boxed{\overline{u_S} \rightarrow \pm 10.8\%}$

$\hookrightarrow$ Normalised conductivity (no geometrical factor) $\frac{\kappa(T)}{\kappa(300\ K)} \rightarrow \quad \overline{u_S} \sim \pm 5.3\%$

ASTM E1228: round robin

$\boxed{\overline{u_S} \rightarrow \pm 6.8\%}$

Thermal conductivity

Therefore:

- Reproducibility (Round robins) : ≳7%
- Instrumental: ≳ 2%

(Guarded hot plate)

Combined Uncertainty ≳ 7.3%

Combined Uncertainty ≳ 10%

(Other methods → + ref. sample)

IEA results:
Specific heat for n-type half-Heusler

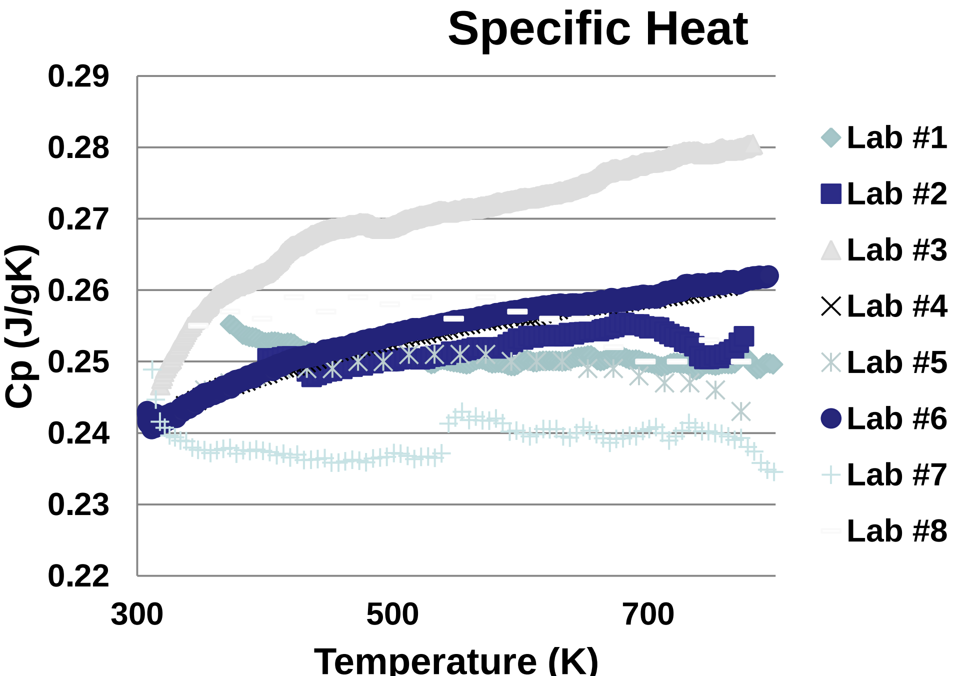


Figure of merit

Seebeck: U $\gtrsim +6/\text{-}14\%$

Resistivity: U $\gtrsim 10\%$

Thermal conductivity: U $\gtrsim 7\%$

➔ ZT: U $\gtrsim +15/\text{-}23\ \%$

(Uncertainty in T not included)

Thermal conductivity: U $\gtrsim 10\%$ ➔ ZT: U $\gtrsim +17/\text{-}25\ \%$

(Uncertainty in T not included)

Improving uncertainty

- Instrumental: more accurate equipment
    - smaller instrumental error
    - smaller random error

      (**better repeatability and reproducibility)**

- Repeatability → take more measurements!
- Reproducibility → do more experiments!

$$\boxed{\bar{\sigma} = \frac{\sigma}{\sqrt{N}}}$$

Key points to remember

- **Every measurement is subject to some uncertainty.**
- *Guide to the Expression of Uncertainty in Measurement freely available on BIPM website http://www.bipm.org/en/publications/guides/gum.html*

- **A measurement result is incomplete without a statement of the uncertainty.**

- **When you know the uncertainty in a measurement, then you can judge its fitness for purpose.**

- **Understanding measurement uncertainty is the first step to reducing it**

- **Material properties will carry uncertainties in perc**
  ±25%
- **Precision vs trueness**

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'Measure thrice, cut once'. You can reduce the risk of making a mistake by checking the measurement a second or third time.