2011 Measurement Science Conference

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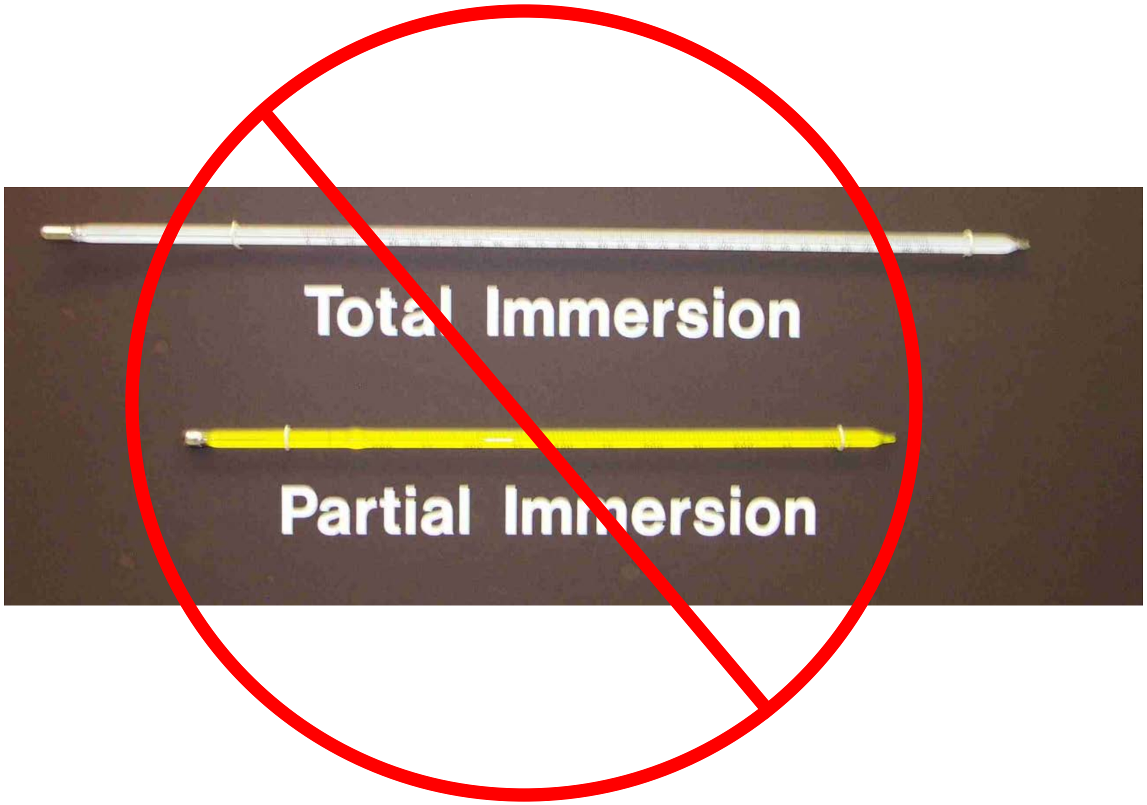
NIST

Sensor Science Division

NIST
National Institute of Standards and Technology
U.S. Department of Commerce

PML PHYSICAL MEASUREMENT LABORATORY

Replacing "Banned" Mercury-in-Glass Thermometers



Technical Contacts

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Interstate Mercury Education & Reduction Clearinghouse (IMERC)

- **Starting in 1999 the states in the Northeast and other parts of the country actively began to**
  - Pursue enactment of legislation focused on reducing Hg in products and waste
  - Provide ongoing technical and programmatic assistance to states that have enacted Hg education and reduction legislation
  - Provide a single point of contact for industry and the public for Hg education and reduction programs
  - promote consistency among the states in implementing product bans
  - provide a single point of contact for manufacturers.
- **The IMERC state members include**
  - California, Connecticut, Illinois, Louisiana, Maine, Massachusetts, Minnesota, New Hampshire, New Jersey, New York, North Carolina, Rhode Island, Vermont, and Washington.
- **Example of state law (New York – 1/08)**
  - Cannot sell, offer for sale, or distribute mercury-added thermometers if a non-mercury alternative is available; excludes mercury-added thermometers that are a component of a larger product in use prior to January 1, 2008 or resale manufactured before January 1, 2008; excludes if the use is a federal requirement

http://www.newmoa.org/prevention/mercury/imerc.cfm

General Issues with Replacing Mercury-in-Glass Thermometers

- **Hg-in-Glass thermometers are in widespread use:**
  - Food processing, laboratory use, health care, petroleum testing, etc.
- **New regulations strictly controlling either sales or use of instruments containing Hg and the high cost of mitigating mercury spills are driving the replacement of most Hg thermometers**
  - Interstate Mercury Education & Reduction Clearinghouse (IMERC)
  - Clean-up of mercury spills can cost from $2,000 to $10,000
- **The use of mercury thermometers is specified in government regulations (e.g., FDA) and in hundreds of documentary standards**
  - Over 800 ASTM standards incorporate a mercury-in-glass thermometer
- **Hurdles for the adoption of alternatives to Hg thermometers**
  - Existing regulations that mandate Hg thermometers
  - Alternative thermometer must be shown to have satisfactory performance for the application
  - User community needs assistance in the choice and use of the appropriate alternative technology.

Possible Replacement Thermometer Types

Analog Possibilities:

Organic Liquid-in-Glass Thermometers

–196 °C to 200 °C

Proprietary Liquid-in-Glass Thermometers

–200 °C to 300 °C

Digital Possibilities:

Digital Readout with Probe

–196 °C to 850 °C

> Industrial Platinum Resistance Thermometers (IPRTs)

–196 °C to 850 °C

> Thermistors

–50 °C to 100 °C

> Thermocouples

–196 ° C to 2100 °C

Considerations in Selecting a Thermometer

Digital or Analog: **Compliant with ASTM standards, internal measurement procedures, and training in use**

Accuracy: Uncertainties range from < 0.1 m°C to >1 °C

Cost of Thermometer: Range from \$6 to \$6000

Cost of Calibration: from \$50 to \$12,000

Temperature Range of measurement

Stability and Durability during use

- **chemical contamination**
- **resistance to high temperatures, moisture, vibrations, and shock**

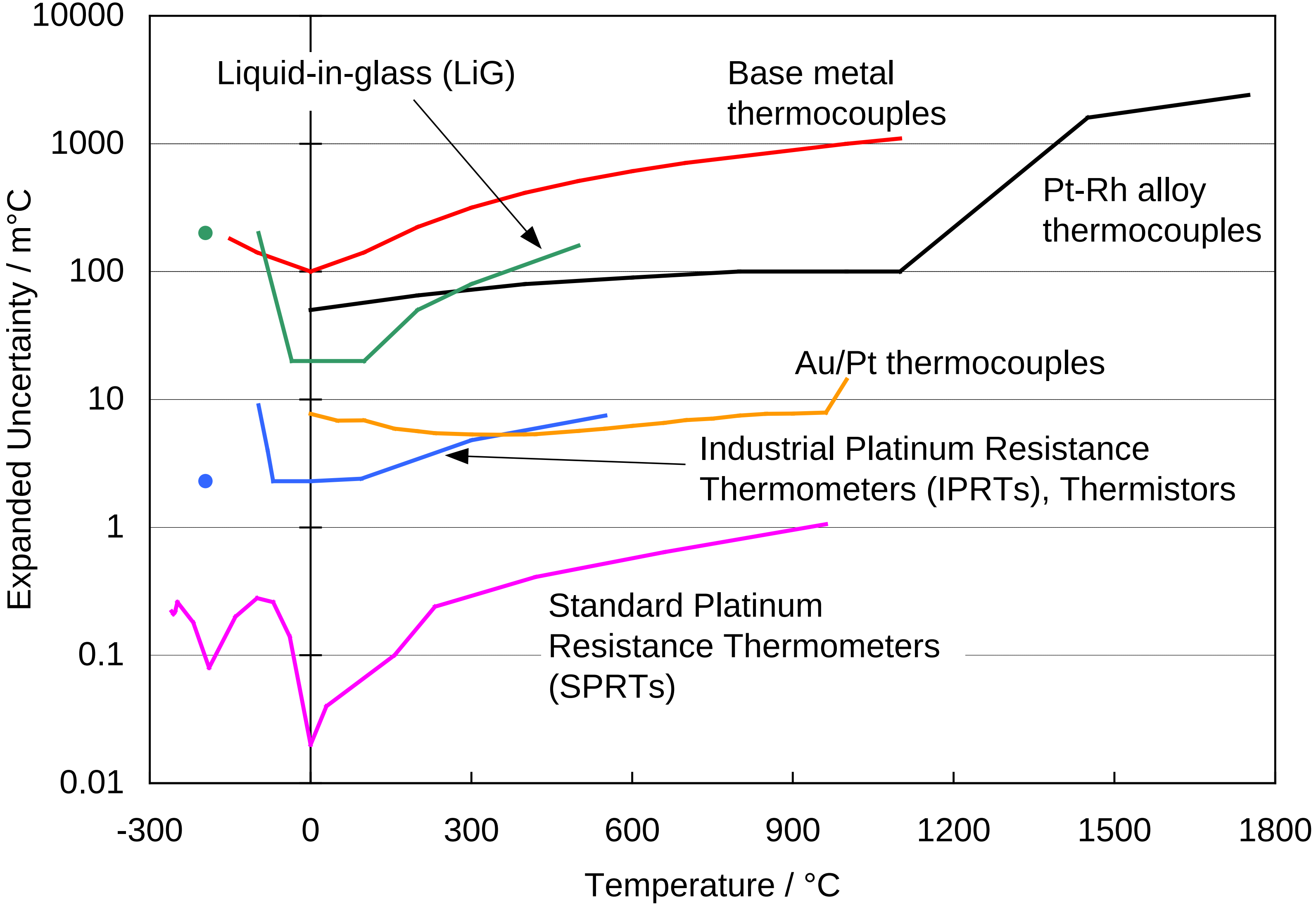
Compatibility with measurement equipment

- **resistance thermometers, thermocouples easy to integrate to electronics**
- **liquid-in-glass, digital thermometers much easier for quick visual inspection**

Compatibility with object being measured

- **sheath diameter, length chosen for good thermal equilibrium**

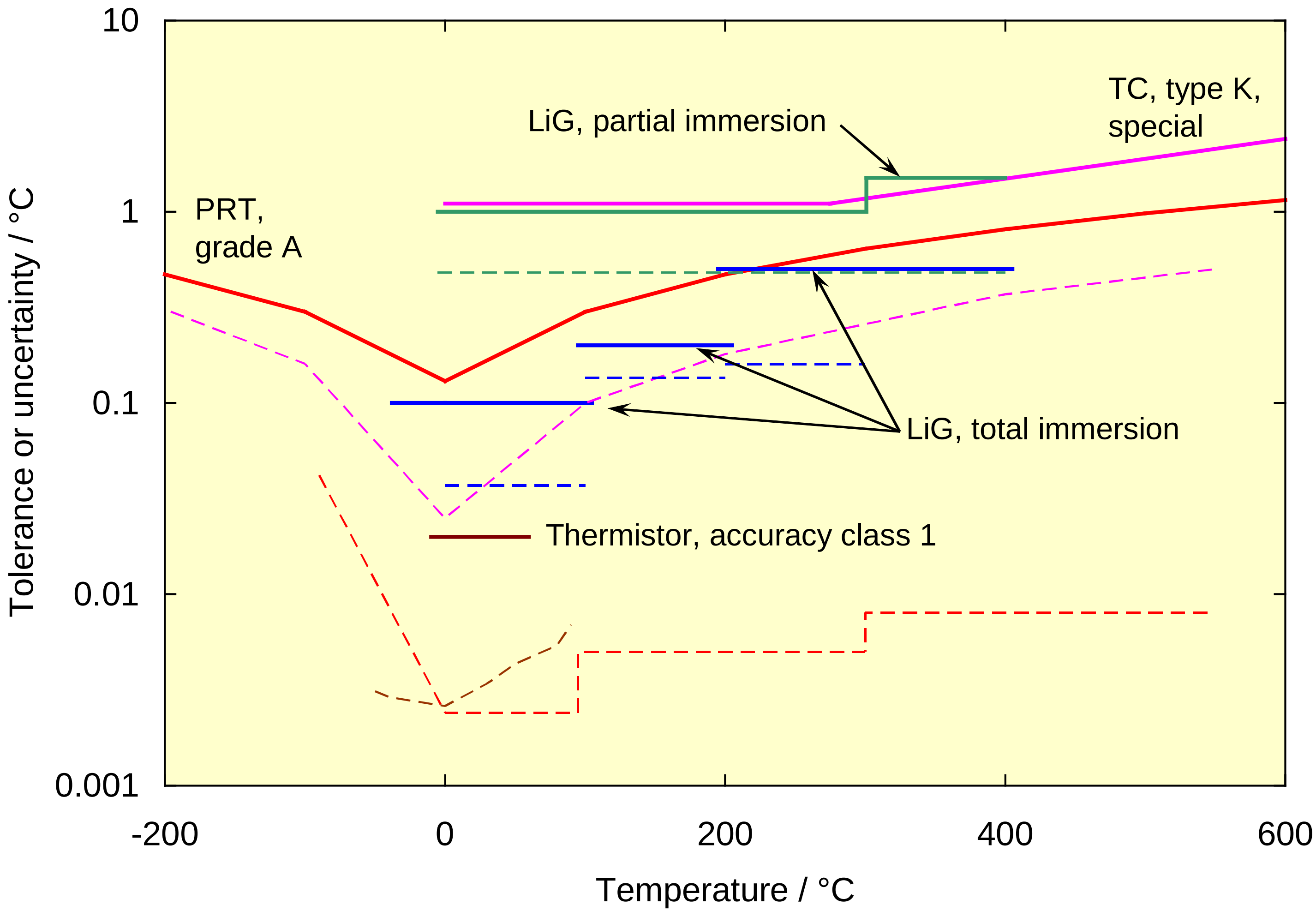
Thermometer Types: Calibration Ranges and Uncertainties



Comparative Thermometer Types: Calibration Methods, Uncertainties, and Costs

Thermometer Type	Nominal Cost $	Temperature Range, °C	Calibration Method	Calibration U (k=2), °C	Calibration Cost, $
Digital Thermometer	Uncertainty Driven 50 to 25,000	Depends on Need	System or Separate ?	Depends on How Used	1000
IPRT	100 to 1000	–196 to 500	Comparison	<0.01	1750
Thermistor	50 to 1000	–10 to 100	Comparison	<0.005	1200
Thermocouple, Noble Metal	600	0 to 1100	Comparison	0.3	1000
Thermocouple, Base Metal	6 to 50	0 to 1100	Comparison	1	1000
Organic LiG	30	–196 to 200	Comparison	<2	1000

Tolerances vs. Calibration Uncertainties



Colored lines: ASTM tolerances (ASTM E1, E1137, E230, and E879).

Dashed lines: NIST calibration uncertainties (*k*=2)

Tolerances vs. Calibration Uncertainties

Tolerance band: manufacturer's guarantee that the instrument response will conform to a standard response function to within an error equal to the tolerance.

Calibrated thermometer: may or may not have a response close to the nominal response function for that thermometer type.

Response of individual unit is reported, along with uncertainties of the calibration process.

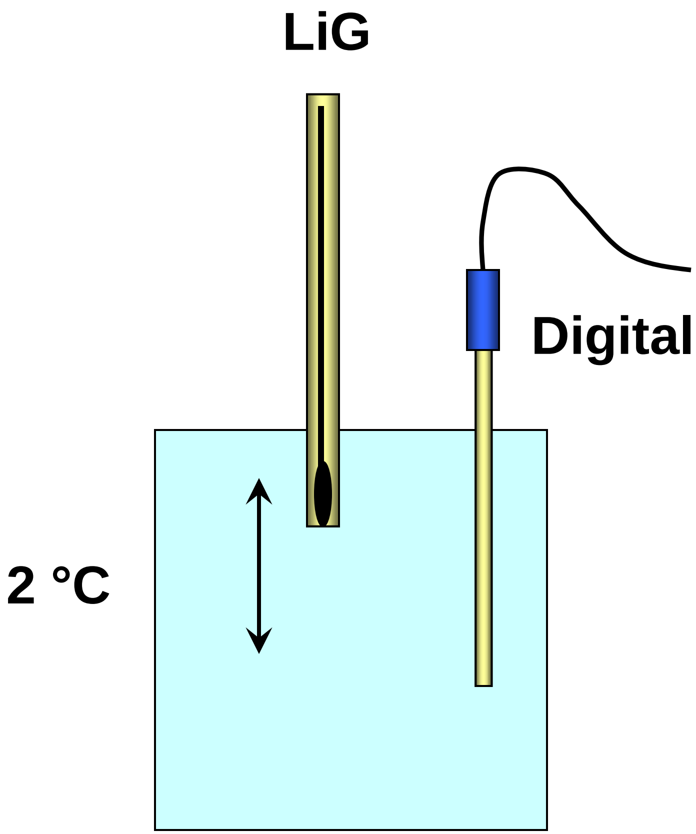
Individually calibrated thermometers cannot be considered directly interchangeable, unless the readouts or software are adjusted to incorporate the individual response function.

Temperature Non-Uniformity

Total-Immersion Liquid-in-Glass Thermometer: Immersion depth varies with temperature

Partial-Immersion Liquid-in-Glass Thermometer: Immersion depth specified on thermometer

Digital Thermometer: Placing thermometer at a fixed depth may introduce a bias, due to temperature variations in apparatus



Bias of Liquid-in-Glass Thermometers

1. For a partial immersion thermometer, if the **stem temperature during use differs significantly from the ASTM E 1 stem temperature** specified in Table 4 of E 1 and a correction is not applied, there will be an error (see ASTM E 77).

2. **Total-immersion thermometer is used at a fixed, partial immersion, with no correction applied.** Extreme care must be taken in selecting an alternative thermometer for these applications, because use of a different thermometer type, while reducing the measurement error, may cause changes in the bias of the standard.

3. **If the thermometer is not in good thermal contact with the body being measured**, there may be significant errors due to thermal conduction along the thermometer sheath. Temperature reading biased even though the precision is acceptable.

Typical Measurement Uncertainty Budget: Thermocouples

Component	Method of evaluation
Calibration uncertainty or tolerance	Manufacturer or calibration laboratory, or ASTM E 230 tolerance
Thermocouple drift	Results from literature, or in situ comparisons
Reference junction uncertainty	Manufacturer or independent evaluation
Readout uncertainty	Manufacturer or independent evaluation
Readout drift	Manufacturer or independent evaluation

Items in italics—examples of components generally not addressed with liquid-in-glass thermometers

Examples of Subtle Device/Readout Failures

Long-term drift of readouts is expected, and addressed by periodic recalibration, but there are other risks:

- Device loses calibration values in memory & reverts to default coefficients
- Resistance bridge balances correctly, but circuitry to compensate for cable resistance is faulty
- Incorrect entry of calibration coefficients into readout
- Probes switched without updating coefficients

Consequence: Greater need for measurement cross-checks / measurement assurance / check standards

- Routine checks of performance
- Checks at ice point
- Comparison of readings of different thermometers

Non-Mercury Liquid-in-Glass Thermometers

- **Organic liquids generally have inferior performance to mercury,** but are a reasonable alternative if uncertainty requirements are modest (ASTM standard just begun)
- **Beware of drainage of organic liquid down capillary wall on cooling**
- **"Next-generation" proprietary liquids under development** (Existing ASTM standard E2251); good accuracy, but check for separation of liquid column
- **For all non-mercury LiG thermometers,** capillary and bulb dimensions will be different, with different time response and immersion characteristics!!!
- **Uncertainties are not well understood – so far**
  - NIST Thermometry Group (Dawn and Wyatt) are measuring **organic** LIGs to determine uncertainty
    - Both **calibration** and **repeatability in use** uncertainties

Choice of a LiG Thermometer

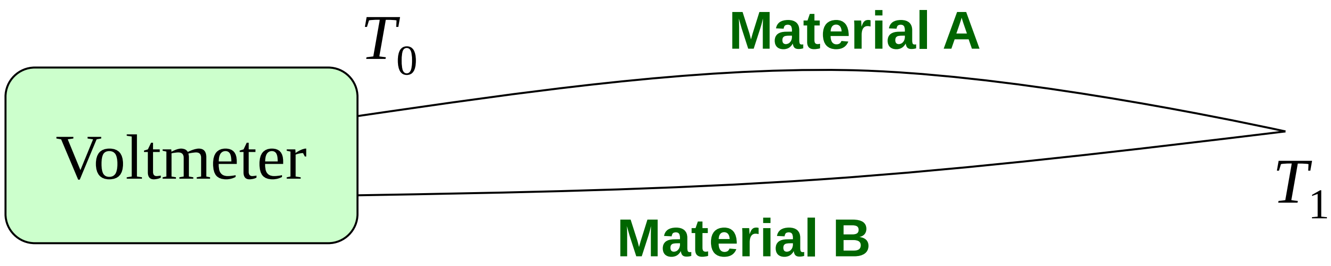
Advantages of LiG thermometers

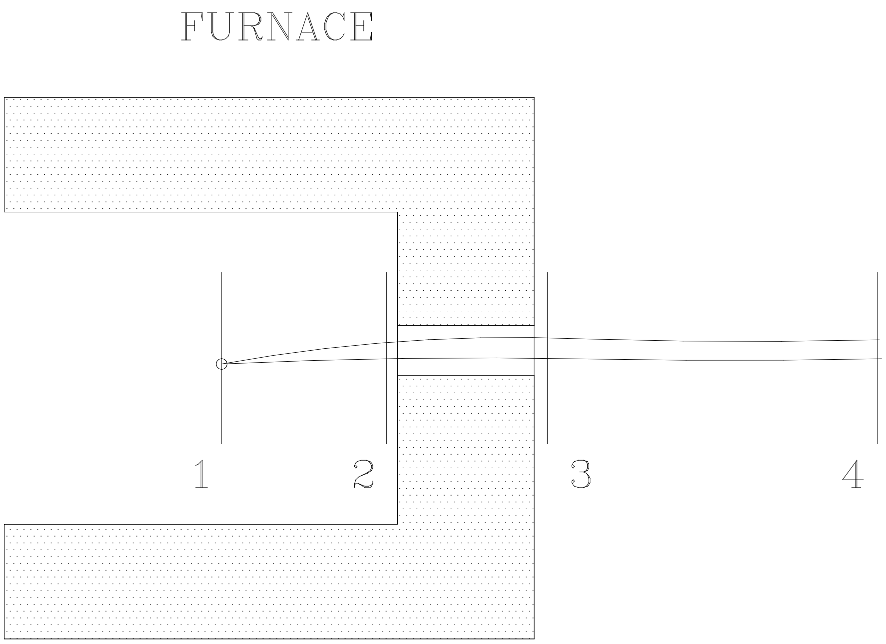
- Relatively inexpensive
- When used at moderate temperatures (<150 °C), recalibration at the Ice MP suffices
- Damage to thermometer is usually visually apparent (!!!)

Disadvantages of LiG thermometers

- Very difficult to automate
- Total immersion require adjustment of immersion with changing temperature/Partial immersion not too accurate
- Hg is banned in some circumstances; prohibitively expensive to clean up in other instances

Thermocouples...any two dissimilar conductors, joined at one end





Although total signal depends on temperature of two ends (1 & 4), thermocouples generate signal primarily in regions of strong thermal gradients. (Region 2-3)

The junction itself does not generate a voltage!!

Advantages of Thermocouples

- Cheap
- Wide temperature range (–270 °C to 2100 °C)
- Small (down to 0.25 mm diameter)
- Easy to integrate into automated data systems

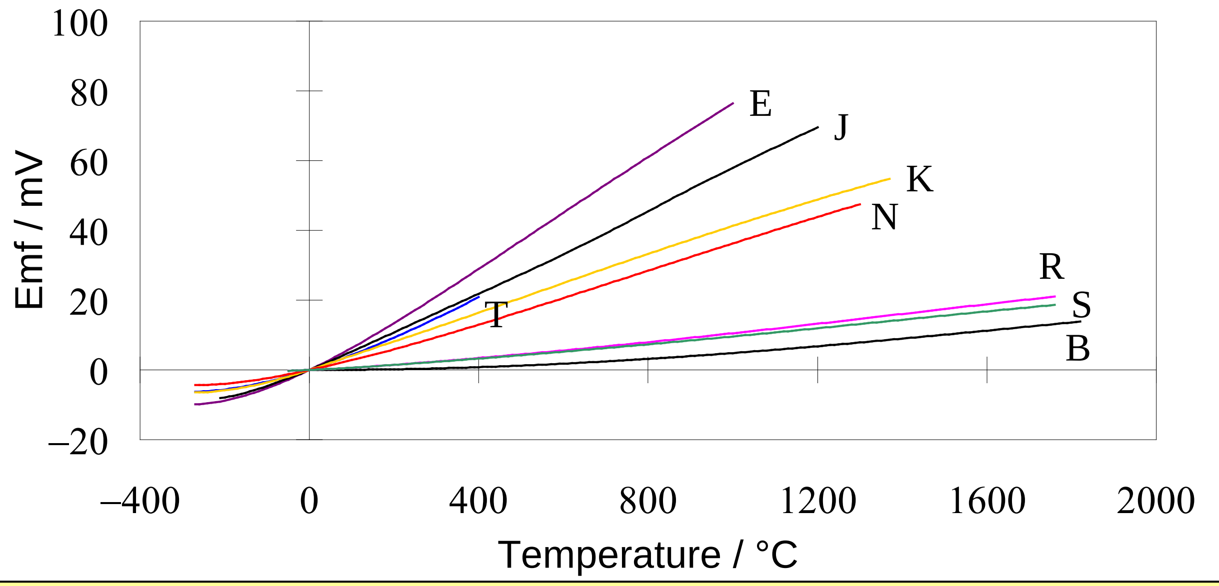
Disadvantages of Thermocouples

- Small signals, limited temperature resolution (1 mK to 1 K)
- Thermocouple wires must extend from the measurement point to the readout. Signal generated wherever wires pass through a thermal gradient.
- At higher temperatures, thermocouples may undergo chemical and physical changes, leading to loss of calibration.
- Recalibration of certain thermocouples or in certain applications is very difficult.

Care and Feeding of Thermocouples

- Monitor drifts in base metal thermocouples by *in situ* tests
- Protect from mechanical strain and kinks
- Protect from contamination using alumina or silica tubes, or use mineral-insulated-metal-sheathed thermocouples.
- For each temperature environment to be measured, a new thermocouple should be made, and it should always be used at the same immersion.
- Obey the ASTM upper temperature limits for bare wire thermocouples.

8 Letter-Designated Thermocouple Types



type E: High Seebeck coefficient, homogeneous materials. Good for low temperatures.

type J: Cheap!

type K: Fairly cheap high temperature thermocouple.

type N: Good base metal thermocouple for high temperatures.

type T: Homogeneous materials. Direct connection of differential pairs to voltmeters.

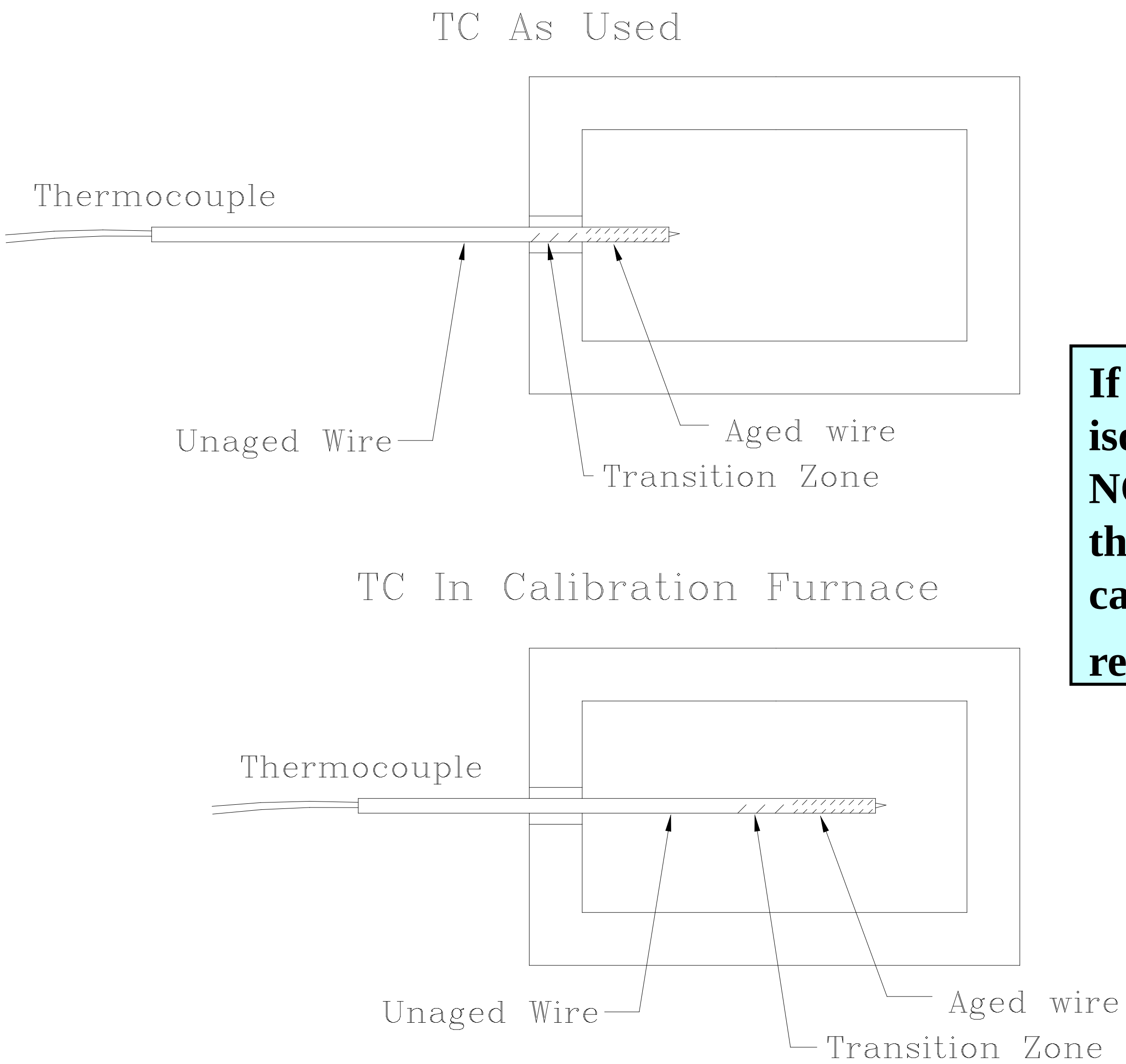
Use type K, E, or T at room temp., type K up to 200 °C, type N in the range 300 °C to 600°C, type N or K above 600 °C

type R, S: Noble metal thermocouple for range 0 °C to1400 °C.

type B: Noble metal thermocouple used from 800 °C to 1700 °C.

Use type R or S below 1300 °C, type B above 1300 °C.

Recalibration of Used Thermocouples is Problematic!

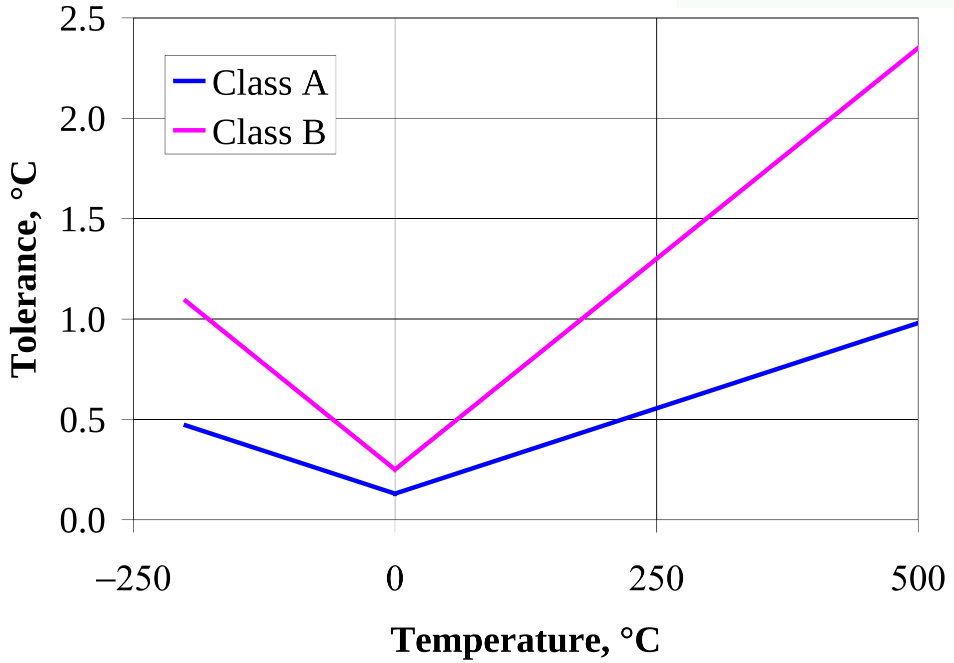


If the furnace is isothermal, there will be NO difference between the original TC calibration and the recalibration.

Industrial Platinum Resistance Thermometers
IPRTs

- > **Bare element or probe configuration**
- > **2, 3, or 4-wire resistance element**
- > **Positive temperature coefficient**
- > **Nominal temperature range of use:**
  - –200 °C to 850 °C
- > **Nominal resistance at 0 °C**
  - 100 Ω

Pictures courtesy of SDI and Minco



ASTM E1137 "Off the Shelf" Tolerance and Uncertainty

Considerations in Selecting IPRTs

ADVANTAGES

- Wide temperature range
- *R* vs. *T* is well characterized
- Rugged construction
- Cost is less than an SPRT
- Available in different shapes and sized to meet most application requirements
- Can be used with a digital temperature read-out device

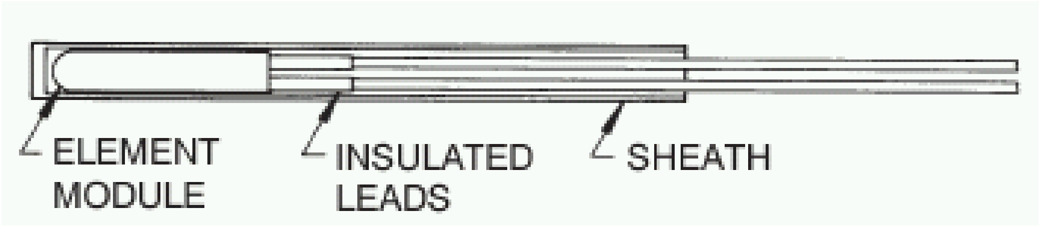
DISADVANTAGES

- Resistance element is not strain free - hysteresis
- Deterioration at elevated temperatures
- 2- and 3- wire devices need lead-wire compensation
- Non-hermetically sealed IPRTs will deteriorate in environments with excessive moisture
- Not as accurate as an SPRT
- **Not a defining standard of the ITS-90**

Influences on PRT Immersion Properties

Construction

- Lead wire gauge and material
- Sensor element length
- Sheath thickness & material
- Diameter



Sensor length can vary from 4 mm to 30 mm

Where is the probe inserted?

- Stirred-liquid baths give excellent heat transfer
- A stagnant air gap has poor heat transfer

- **Consider 1/8” diameter sheaths**
- **Eliminate or reduce air gaps**

Picture courtesy of Minco

Recalibration Interval for an IPRT

Widely varies by design

Widely varying performance based on use

- Thermal history
- Mechanical shock

Behavior is not as predictable as an SPRT

Drift at 0 °C or 0.01 °C does not always correlate well at other temperatures

Recommendation:

- Measurement at 0 °C or 0.01 °C as a minimum
- Adding a measurement at highest temperature of use is better

Thermistors (Thermal Resistor)

Semiconductors of ceramic material

Temperature Range: –50 °C to 100 °C

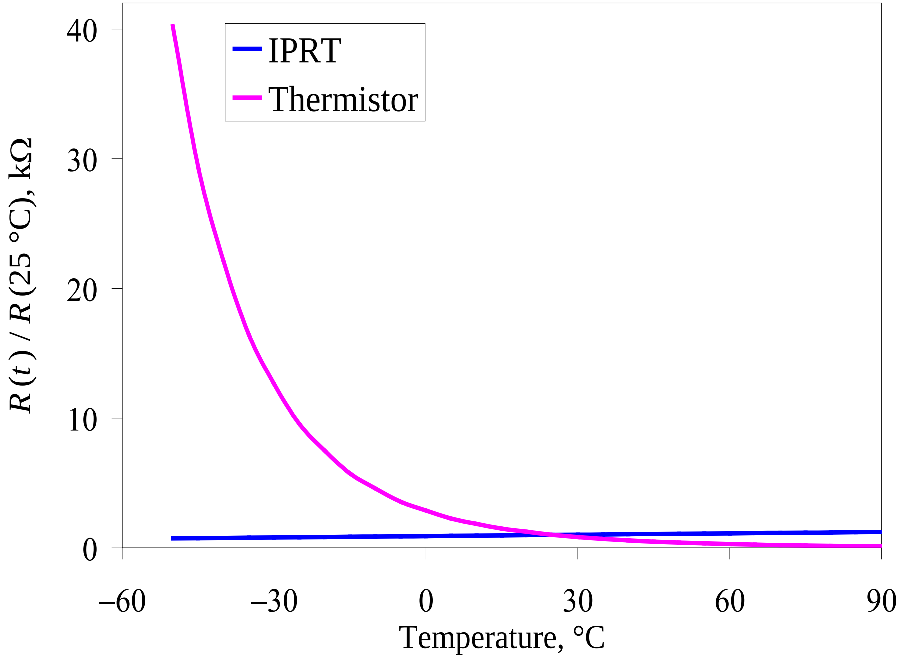
Standard Forms:

bead	encapsulated by epoxy or glass
probe	bead in glass rod
disc	0.5 cm to 1.3 cm thick
washer	2 cm diameter
rod	moderate power capacity

Resistance: 300 Ω to 100 MΩ

Negative Temperature Coefficient

The vast majority of commercial thermistor thermometers are in the NTC category.



Thermistor Sensitivity

– Resistance changes by more than a factor of 300 from –50 °C to 90 °C
– Higher sensitivity than an IPRT
– ***Non-linear***
  - –50 °C: 5000 Ω / °C
  - 90 °C: 8 Ω / °C

Advantages and Disadvantages of Thermistors

ADVANTAGES

Easy to miniaturize
Rugged
Fast response time
Inexpensive
High sensitivity
Small-size beads may be used for point-sensing
Stability: 4000 h at 100 °C

bead-in-glass	0.003 °C to 0.02 °C
disc	0.01 °C to 0.02 °C

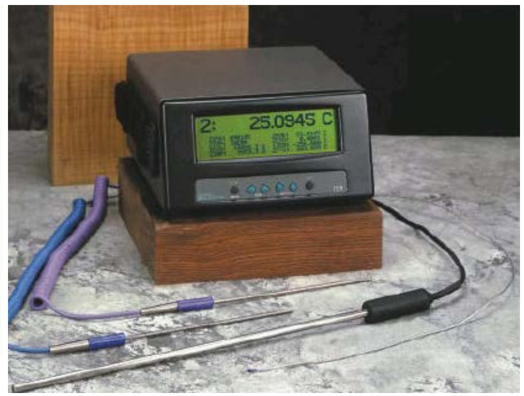
DISADVANTAGES

Small temperature range
Non-linear device
Needs frequent checks on calibration when exposed to t > 100 °C
Interchangeability is limited unless the thermistors are matched
Self-heating may be large

Digital Thermometers

What is a digital thermometer?

– An electronic measurement box that converts either resistance or emf of a thermometer to temperature



Pictures courtesy of Agilent, ASL, Brookstone, Hart Scientific, and Omega Engineering

Digital Thermometers

- **Easy to use in conjunction with an electronic-based thermometer (e.g. IPRT, Thermistor, Thermocouple)**

- **Device displays temperature directly by using the calibration coefficients of the thermometer**
  - Different algorithms available
  - Uncertainty: 0.001 °C to 1 °C
  - Resolution: 0.0001 °C to 1 °C

- **Device may allow two thermometers to connected directly to unit for differential thermometry**

- **Some have software that allow “real time” calibration**

- ***Cost of purchase, training in use, and recalibration are a serious consideration***

Conclusions & Roadmap

1. **Identify the level of uncertainty needed**
2. **Identify the temperature range**
3. **Identify unique aspects of the test apparatus or method** (e.g., inherent temperature non-uniformity)
4. **Identify adequacy of presently specified Hg thermometer** (anywhere from overkill to just adequate)
5. **Make judgments on**

   how tightly to prescribe the thermometer

   whether to require calibration, measurement assurance

   what tests/round robins are needed to validate the revised standard

- When in doubt, call for assistance: Greg or Dawn
- We can't recommend a particular manufacturer, but we can help in determining what type of device should work for your application.

More Information: Gregory F. Strouse, "Selection of Alternatives to Liquid-in-Glass Thermometers," *J. ASTM International* **2**, JAI13404 (2005)