# Transitioning from "Banned" Mercury Thermometers to Alternative Thermometers

Dawn Cross & Wyatt Miller NIST



#### **Technical Contacts**

Dawn Cross, 301 975 4822, dawn.cross@nist.gov

Wyatt Miller, 301 975 3197, wmiller@nist.gov

Greg Strouse, 301 975 4803, gstrouse@nist.gov

# **NIST Hg Reduction Activities**

- Over the last 6 years, NIST has actively participated in several national and international phase-out efforts to identify alternative thermometers for a broad range of measurement applications
- Several U.S. government and state agencies as well as international organizations are driving the removal of Hg thermometers as a means to reduce mercury in the environment
  - NIST Environment Compliance Group
  - EPA Office of Pollution Prevention and Toxics
  - Northeast Waste Management Officials' Association (NEWMOA) Interstate Mercury Education & Reduction Clearinghouse (IMERC)
  - American Petroleum Institute (API)
  - ASTM International
  - United Nations Environment Programme (UNEP) UNEP Global Mercury Partnership

# **NIST Hg Reduction Activities**

- NIST stopped calibrating Hg thermometers on March 31, 2011
  - The use of Hg thermometers has been virtually eliminated in routine hospital use, but a wide variety of regulations and test methods in the petroleum industry continue to specify mercuryin-glass thermometers.
  - NIST will continue to support our stakeholders by providing technical and scientific support to find suitable alternative thermometers that meet their measurement needs
  - NIST still calibrates all other types of thermometers
    - Fees are at least 20% less than in 2010
    - Increased automation = decreased turn-around time

#### **NIST Industrial Thermometer Calibration Services**

#### **Industrial Platinum Resistance Thermometers (IPRTs)**

-196 °C to 550 °C

#### **Thermistors**

-50 °C to 100 °C

#### **Thermocouples**

-196 ° C to 2100 °C

#### **Organic/Proprietary Liquid-in-Glass Thermometers**

-196 °C to 200 °C

#### **Digital Thermometers**

-196 °C to 550 °C

Calibration fees are now 20% lower than in 2010 !!!

# **ASTM E20 Activities in Hg Thermometer Reduction**

- E20.05
  - Hg Reduction Initiative
    - Chair, D. Cross
- E20.09 Standard Guide for Digital Contact Thermometers
  - Chair, G. Strouse (NIST)
  - Task Group Chair, C. Meyer (NIST)

This Guide describes general-purpose, digital contact thermometers (hereafter simply called "digital thermometers")... The different types of temperature sensors for these thermometers are described, and their relative merits are discussed. Nine accuracy classes are proposed for digital thermometers; the classes consider the accuracy of the sensor/measuring-instrument unit...

This Guide provides a number of recommendations for the manufacture and selection of a digital thermometer...

#### 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

# **United Nations Environmental Program - Hg**

- International Treaty on Hg
  - Includes eventual elimination of Hg products
    - Reducing mercury in products may be the most effective means to control mercury in waste. Clear regulation can prompt manufacturers to produce mercury-free products.
- Anticipated effective date of 2013
- United States of America is a contributing signatory
  - Cooperative government agency effort
    - NIST representatives: D. Poster and G. Strouse

## Why Replace Hg Thermometers?

- Mercury is a neurotoxin
  - Everyone is at risk from ingestion exposure to mercury
  - Mercury poisoning symptoms include:
    - Tremors
    - Emotional changes
    - Insomnia
    - Neuromuscular changes
    - Performance deficits on tests of cognitive function
    - Increase exposure may cause kidney failure, respiratory failure and death
- Broken thermometer can cost a significant amount of money
  - Typical cost is \$5K to \$20K
  - Extreme cost is \$1M
- Several U.S. government, state agencies, and international organizations are driving the removal of Hg thermometers as a means to reduce Hg in the environment.

#### **Measurement Truths to Consider**

#### Accuracy

- Hg thermometers are not more accurate than alternatives
- ASTM standards give "out-of-the-box" tolerance specifications for Hg and alternative thermometers
  - Specifications can be used for interchangeability

#### Cost

• Hg thermometers are not cheaper when you consider clean up

#### Calibration

- All thermometers need calibration
  - All thermometers need verification often
  - Verification for all industrial thermometers starts with the ice melting point

#### Range of use

 Digital thermometers cover the range from at least –200 °C to 500 °

# **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** 

-196 °C to 300 °C

## Digital Possibilities:

Digital Readout with Probe

-196 °C to 2100 °C

- > Industrial Platinum Resistance Thermometers (IPRTs)
  - -196 °C to 500 °C
- > Thermistors
  - -50 °C to 100 °C
- > Thermocouples
  - -196 ° C to 2100 °C

# **Quick Tutorial on Electronic-Baseed Industrial Thermometer Sensors**

**Industrial Platinum Resistance Thermometers** 

**Thermistors** 

**Thermocouples** 

# What is an Industrial Platinum Resistance Thermometer (IPRT)?

- 2, 3, or 4-wire resistance element nominally 100  $\Omega$  @ 0 °C
  - Wire wound
  - Thick film
  - Thin film

Resistance changes as a function of temperature

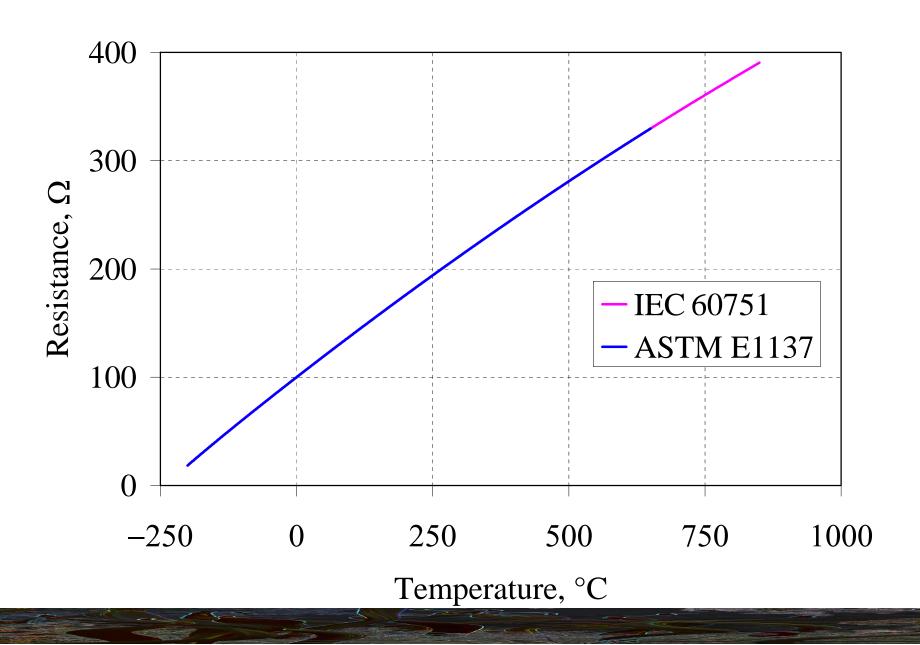
Positive temperature coefficient
Nominal temperature range of use:

– 200 °C to 850 °C

Nominal resistance at 0 °C

 $-100 \Omega$ 

# Nominal Resistance vs. Temperature Curve for an IPRT



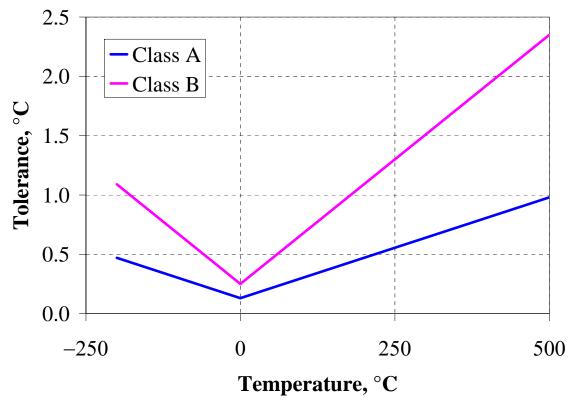
# **IPRT Reference Functions and Standards**

	$R(0^{\circ}C)$ , $\Omega$	alpha, Ω/Ω/°C	range, °C		
<b>IEC 60751</b>					
class AA	100	3.85 x 10 <sup>-3</sup>	-200 to 250		
class A	100	3.85 x 10 <sup>−3</sup>	-100 to 450		
class B	100	3.85 x 10 <sup>-3</sup>	-196 to 600		
ASTM E1137 – USA Standard					
class A	100	3.85 x 10 <sup>-3</sup>	-200 to 650		
class B	100	3.85 x 10 <sup>−3</sup>	-200 to 650		

IEC = International Electrotechnical Commission
ASTM = American Society for Testing and Materials

# **ASTM E1137 "Off the Shelf" Tolerance and Uncertainty**

Class A ±[0.13 + 0.0017  t ] °C				
Temperature °C	Tolerance $\Omega$	Tolerance °C		
-200	0.20	0.47		
0	0.05	0.13		
500	0.33	0.98		
Class B ±[0.25 + 0.0042  t  ] °C				
Class B ±	0.25 + 0.004	2  t  ] °C		
Temperature °C	$\begin{array}{c} 0.25 + 0.004 \\ \hline \text{Tolerance} \\ \Omega \end{array}$	Tolerance °C		
Temperature	Tolerance	Tolerance		
Temperature °C	Tolerance Ω	Tolerance °C		



#### **ASTM E1137 vs ITS-90**

#### ITS-90 Equations may be used with IPRTs

# No specific evidence that using ITS-90 equations is better than ASTM E1137 equations

Use extra calibration points to determine uncertainty

# Some measurement equipment may only allow for either ASTM E1137 or ITS-90 equations and not both

End user must decide which works for their purpose

#### Measurement Uncertainties are a function of

- calibration uncertainty
- temperature range of use
- number of calibration points for ASTM E1137 equation
- mechanical vibration
- measurement system
- thermal environment

## **Types and Construction of IPRT elements**

#### Wire-wound element

- Alumina insulator: –200 °C to 850 °C
- Glass insulator: –200 °C to 400 °C
- -2, 3, or 4-wire device

#### **Support of winding**

- None
- Loose MgO powder
- Compacted MgO powder

#### **Sealing**

- None
- Hermetic via glass compound

# **Types and Construction of IPRT elements**

#### Thick and Thin Film element

- Alumina substrate: –200 °C to 850 °C
- Polyimide: -200 °C to 200 °C
- -2, 3, or 4-wire device

#### **Support of winding**

- Not strain free
- Thin film is bendable (strain sensor)

#### **Sealing**

- Hermetic via glass compound for alumina
- Hermetic via polyimide seal

# **Selecting an IPRT**

#### Type – many shapes and sizes to meet most applications

- Bare element
- Probe

#### **Application of use**

#### Temperature range of use

### **Uncertainty in use**

- Tolerance
- Interchangeability

#### **Stability**

#### **Calibration**

- Requirements
- Cost

#### **Environment**

#### Cost

- IPRT
- Measurement Equipment
- Calibration

# "Simple" Questions to Consider in Buying an IPRT

#### **Temperature Range**

- probe, head, and wire compatibility

#### **Specifications of probe**

- Diameter
- Length
- Type of sensor and support
- Number of wires and insulation type
- Type of end seal

#### **Uncertainty**

- In use at your facility
- Stability (e.g. 10 thermal cycles)

#### **Environmental Conditions**

Pressure, vibration, moisture

#### Pt purity – $\alpha$

- 385, 390, 392

#### **Time Response**

#### **Calibration**

- "Off the Shelf" Tolerance and Interchangeability
- Actual calibration Lower Uncertainty

#### Which IPRT Should I Use?

#### Probes recommended for Digital Thermometers

Film IPRTs: good time response, small size, shock resistant

Wire-wound IPRTs with constrained coils: low accuracy, but shock resistant

Wired wound IPRTs with slightly constrained coils: best accuracy (approaching ±0.01 °C over 400 °C span), sensitive to shock. Performance is highly variable with model.

#### **Resistor configuration**

- 2-wire for non-demanding applications (±5 °C)
- 3-wire for ±1 °C measurements, or ±5 °C over long cables
- 4-wire for all high-accuracy measurements

"You get what you pay for - most of the time"

## **Commercial Measurement Equipment & Software**

#### **Digital Readout**

- Accepts ASTM E1137 or ITS-90 coefficients
- Multiple IPRTs possible with scanner
- Differential temperature measurement
- Uncertainty is a function of cost, resolution, stability, and calculation of temperature

#### Multimeter

- 6.5 to 8.5 digit
- May accept ASTM E1137 or ITS-90 coefficients
- Uncertainty is a function of cost, resolution, stability, method of use, excitation current, and in some cases the calculation of temperature

Separate software available from various thermometer vendors

Important to validate the calculation of temperature of either the digital readout, multimeter, or software

# **Sources of Errors When Using IPRTs**

#### **Stability**

- Repeatability at 0 °C or 0.01 °C

#### **Immersion**

- Check immersion characteristics of IPRT on insertion in thermal environment
- Critical for Dry Well Block Calibrators with only 6" immersion depth

#### **Insulation Resistance**

- $-R(22 \text{ °C}) > 100 \text{ M}\Omega$  at 50 V dc is equivalent to 0.1 m°C error
- May degrade at t > 500 °C and high-moisture environments

#### **Self Heating**

- Calibration and measurement current must be the same (nominally 1 mA)
- Thermal contact with temperature of interest is important
- Air probe or fluid probe will influence calibration method

#### **Mechanical Shock and Vibration**

- Vibration or dropping the IPRT will cause the IPRT to drift or fail

#### 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 may not always correlate well at other temperatures

#### **Recommendation:**

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

# **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 sizes application specific
- Can be used with a digital temperature read-out device

#### > DISADVANTAGES

- Mechanical shock and vibration will cause drift
- Deterioration at elevated temperatures (e.g., >500 °C)
- 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

# **Thermistors (Thermal Resistor)**

Semiconductors of ceramic material made by sintering mixtures of metallic oxides such as manganese, nickel, cobalt, copper, iron and uranium.

**Temperature Range**: −50 °C to 100 °C

#### **Standard Forms:**

bead 300  $\Omega$  to 100 M $\Omega$  bead in glass rod

**disc** 0.5 cm to 1.3 cm thick,  $5 \text{ k}\Omega$  to  $10 \text{ k}\Omega$ 

washer 2 cm diameter

**rod** moderate power capacity,  $1 \text{ k}\Omega$  to  $150 \text{ k}\Omega$ 

NTC: Negative Temperature Coefficient - The vast majority of commercial

thermistors used as thermometers are in the NTC category.

**PTC:** Positive Temperature Coefficient - Specialized use over very narrow

temperature ranges, primarily as control and safety devices.

# **Applications for Thermistors**

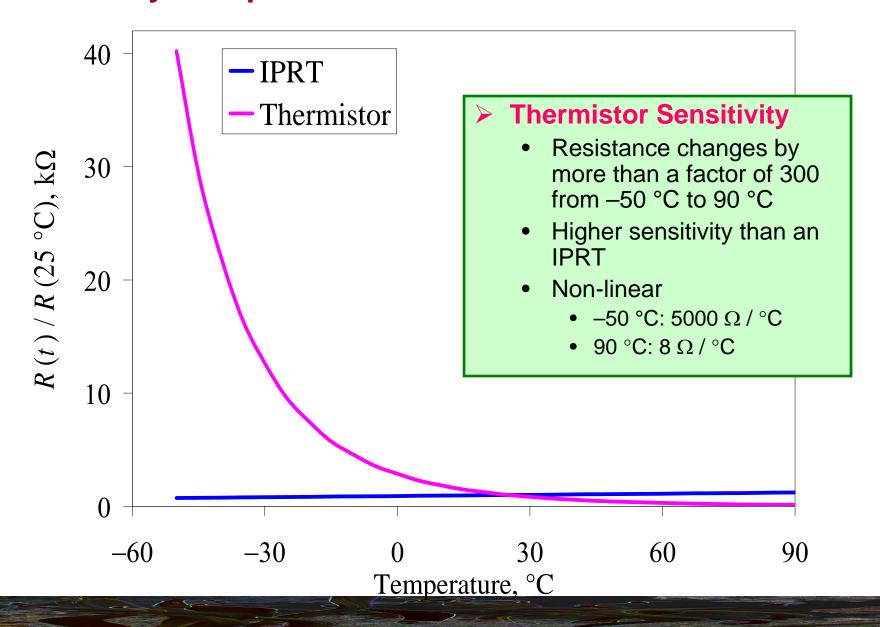
**Application:** temperature measurements, temperature compensation in electrical circuits, temperature control, liquid-level measurements, power measurements, thermal conductivity, biomedical applications and power level control

- High stability if used over a narrow temperature range of 0 °C to 50 °C
- Interchangeable to within 50 mK
- Glass-coated bead for use from 0 °C to 30 °C
- Uncertainties < 1 mK</li>

#### Calibration

- Comparison with reference thermometer
- Fixed-point cells (e.g. small NIST SRM cells or small commercial cells)

# **Sensitivity Comparison between Thermistors and IPRTs**



# Interchangeability of a Thermistor

# Thermistors are interchangeable to within the manufacturer's tolerance band

#### Practical limits from -80 °C to 105 °C

- ±0.05 °C for a 50 °C span
- ±0.10 °C for a 75 °C span
- ±0.20 °C for a 100 °C span

# For a greater accuracy than the tolerance band, then a calibration must be performed

- 0.001 °C for a 15 °C span
- 0.003 °C for a 70 °C span

# **Advantages and Disadvantages of Thermistors**

#### **ADVANTAGES**

Easy to miniaturize

Rugged

Fast response time

Easy to use

Digital thermometer readout

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

# **Cautions for Using Thermistors**

#### Self-heating error may be large

- Use low current and match calibration and use current
- Calibrate air probe in air-filled glass tube

**Epoxy coated thermistors are susceptible to degradation from moisture** 

Glass sealed thermistors are susceptible to degradation if the lead wires are bent apart at the base of the glass

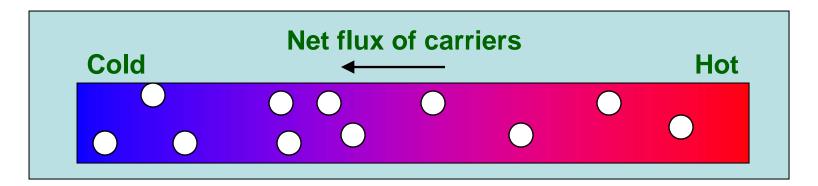
Micro cracks can form in the glass

Heat sink the leads when making electrical connections with solder

#### Do not expose thermistors above 100 °C

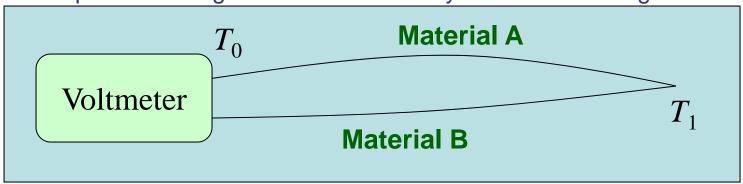
Elevated temperatures will excessively age the thermistor and cause drift

# What is a Thermocouple?



Hotter carriers travel farther before equilibrating with the crystal lattice than cold carriers.

Consequence: charge imbalance when crystal is in thermal gradient.

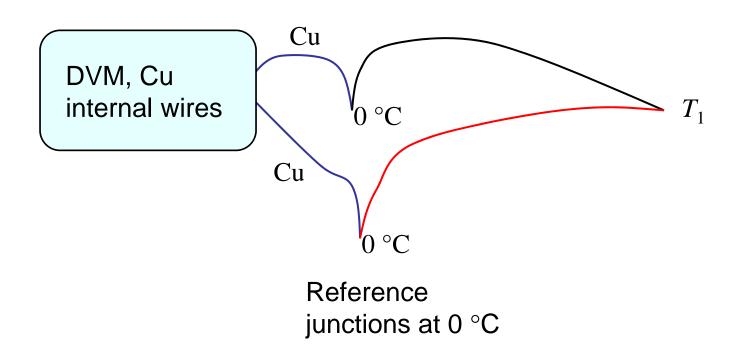


Net electromotive force = emf =  $E = E_A(T_1, T_0) - E_B(T_1, T_0)$ 

# Typical thermocouple circuit

Reference junctions maintained at 0 °C by

- Immersion into ice bath, made from water/ice slurry
- Electronic compensation (typical for Digital Thermometers)



# **Thermocouple Reference Functions**

#### Sources:

 Reference functions for letter-designated TC types in ASTM E230, IEC 584, NIST Monograph 175

Reference functions for non-letter designated types in: ASTM E1751, E988

TC Ref. func. type range, °C		Nominal composition majority component in italics, % in mass	
		Positive leg	Negative leg
В	0 to 1820	platinum-30% rhodium	<i>platinum</i> -6% rhodium
Ε	-270 to 1000	nickel-chromium alloy	copper-nickel alloy
J	-210 to 1200	iron	copper-nickel alloy
K	-270 to 1372	nickel-chromium alloy	<i>nickel</i> -aluminum alloy
Ν	-270 to 1300	nickel-chromium-silicon	nickel-silicon-magnesium
R	- 50 to 1768	<i>platinum</i> -13% rhodium	platinum
S	-50 to 1768	<i>platinum</i> -10% rhodium	platinum
Т	-270 to 400	copper	copper-nickel alloy

# **Selecting a Thermocouple Type**

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.

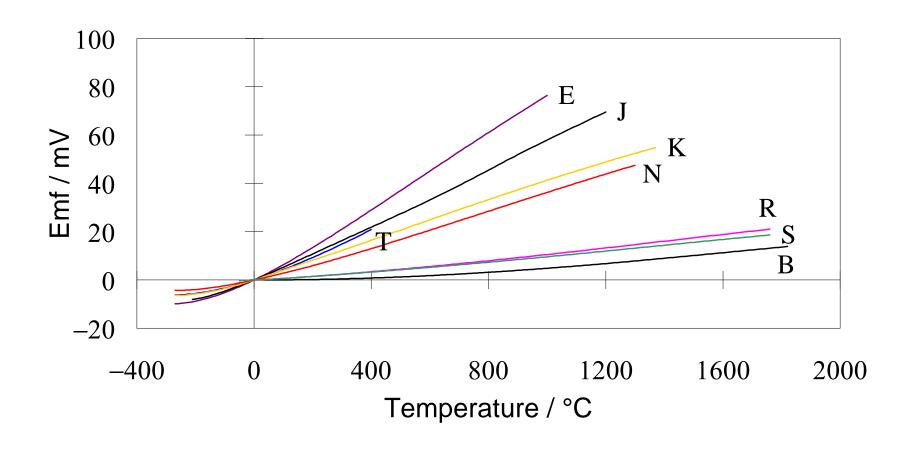
Platinel: High Seebeck coefficient with some of the stability of

types B, R, and S.

Au/Pt: The best accuracy from 0 °C to 1000 °C.

**Pt/Pd:** The best accuracy from 1000 °C to 1500 °C–not commercial

### **Emf-Temperature Relationships for the 8 Letter-Designated Thermocouple Types**



### **Thermocouple Construction Types**

#### Bare wire with ceramic insulators

• the best performance for clean, high temp. environments

#### Soft-insulated wire

- polymer coatings excellent for use up to 200 °C
- fiber-glass insulation, woven ceramic sleeving—fine at moderate temperatures, not good protection at high temp.

### Mineral-insulated, metal-sheathed construction (MIMS):

- excellent for base-metal thermocouples at high temperatures
- excellent for unclean environments
- can be bent to shape

### Bare wire with ceramic insulators, and outer metal sheath

- not flexible
- better contamination resistance and less mechanical strain than MIMS construction for noble metal thermocouples

Thin-film thermocouples: research applications only

### **Bare Wire with Ceramic Insulators**

Weld junction by any method that gives clean, durable joint Flexible sleeving held with heat shrink tubing, or thermocouple plug

- For noble-metal alloys, use high-purity alumina (99 mass% for typical uses, 99.7 mass% for highest accuracy and stability).
- If old insulators are used, avoid cross contamination. e.g.: Pt wire into a bore that held Pt-Rh, or other base metals into bore that held iron
- Above 1300 °C, alumina insulator itself is a source of impurities.
- Use single, unbroken lengths of ceramic, to prevent contamination and loss of volatile alloy components
- Pt-Rh alloys annealed pre or post assembly for best performance

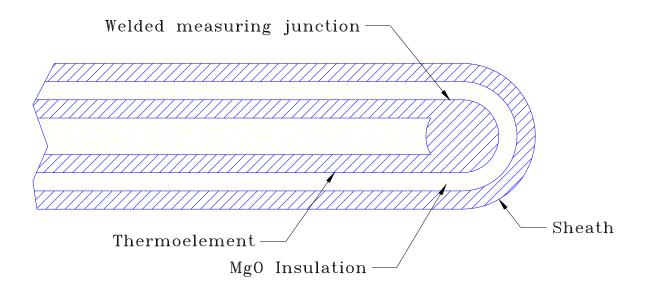
### **Soft-Insulated Thermocouples**

Outer polymer insulation

Weld or solder junction by any method that gives clean, durable joint

- Choose polymer insulation based on upper temperature limit
- Woven ceramics are popular in semiconductor applications
  - Always bake out binders to avoid contamination
  - Contamination of thermocouples by ceramic has not been studied well
  - Use single lengths of alumina in high-gradient zone, if possible

### Mineral-Insulated, Metal-Sheathed (MIMS) Thermocouples



- At high temperatures, choice of sheath material is critical
  - for types K and N, sheath material dominates performance
- MIMS thermocouples are available in small diameters (0.25 mm)
- Sheath protects thermoelements from contamination

### **Thermocouple Color Codes**

TC Type	IEC Positive Cond., Extension Sheath	ASTM Extension Sheath	ASTM Positive Conductor
B E J K N R,S T	— Violet Black Green Orange Brown	Gray Purple Black Yellow Orange Green Blue	Gray Purple White Yellow Orange Black Blue

**IEC:** Negative Conductor is **White** for all Types **ASTM**:

- Negative Conductor is Red for all Types
- For base metal types, duplex insulated thermocouple wire has identical color codes, but with brown overall insulation.

### **Thermocouple Drift Estimates**

### **Base Metal Thermocouples**

- type E, J, N, T: <0.5 °C after 10,000 h at 200 °C
- type J: <0.5 °C after 1,000 h at 430 °C 2 °C after 1,000 h at 650 °C
- type K: <0.2 °C after 10,000 h at 200 °C</li>
   <1 °C after 1,000 h at 650 °C (bare wire, 8 ga)</li>
   up to 4 °C hysteresis, on heating well past 400 °C and then cooling 3 °C after 24 h at 1250 °C (bare wire, 8 ga)
- type N, bare 8 Ga: <1 °C after 24 h at 1250 °C
- "Stabilized" type K & E: <1 °C after 3200 h at 540 °C in air

### **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
- ➤ Adapts easily for use as a Digital Thermometers

### **Disadvantages of Thermocouples**

- ➤ Small signals, limited temperature resolution (1 mK to 1 K)
- > Thermocouple wires must extend from the measurement point to the readout.
- ➤ At higher temperatures (>500 °C), thermocouples may undergo chemical and physical changes, leading to loss of calibration.
- > Recalibration for use above 200 °C is difficult

### What is a Digital Thermometer?

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

• IPRT, Thermistor, or Thermocouple

### **Digital Thermometers**

- > Electronic Display + Probe = Digital Thermometer
- > Easy to use
  - Measurement system adapts to different probe types (e.g., IPRT, thermistor, TC)
  - Hand held, battery operated
  - Connected to a computer
  - Large temperature range
- Device displays temperature directly by using the ASTM coefficients or calibration coefficients of the thermometer
  - ASTM E20 Standards
  - ITS-90
- 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 maintenance are a serious consideration

### **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

### Replacement 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:
  - How to select what type of device should work for your application.
  - How to maintain traceability
  - How to validate accuracy and re-calibration



### **Considerations in Selecting a Thermometer**

Digital or Analog: Compliant with ASTM E20 standards, internal measurement procedures, and training in use

Accuracy: Uncertainties range from 0.01 °C to >1 °C

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

Cost of Calibration: from \$1,000 to \$50

Temperature Range of measurement: varies by thermometer type

**Stability and Durability during use** 

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

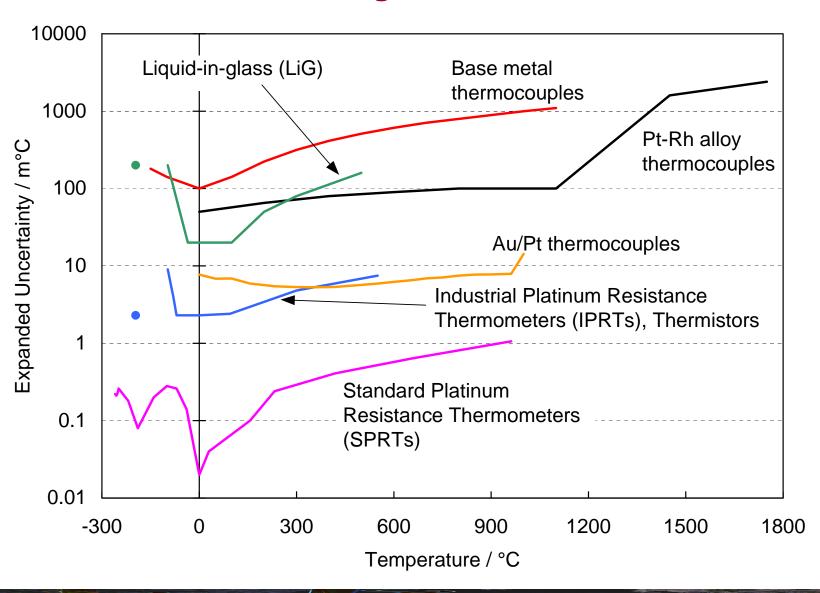
**Compatibility with measurement equipment** 

- Digital probes 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	Probe Type	Nominal Cost, \$	Temperature Range, °C	Calibration Method	Measurement Uncertainty, °C	
Digital	IPRT		-196 to 500		0.01 to 1	
	Thermistor	5 to 1,000	-50 to 100	Comparison	0.005 to 0.01	
	TC		-196 to 2100		0.1 to 1	
Analog	Organic LiG	30	-196 to 200	Comparison	1 to 3	
	Proprietary LiG	50 to 200	-196 to 300		?	

### **Tolerances vs. Calibration Uncertainties**

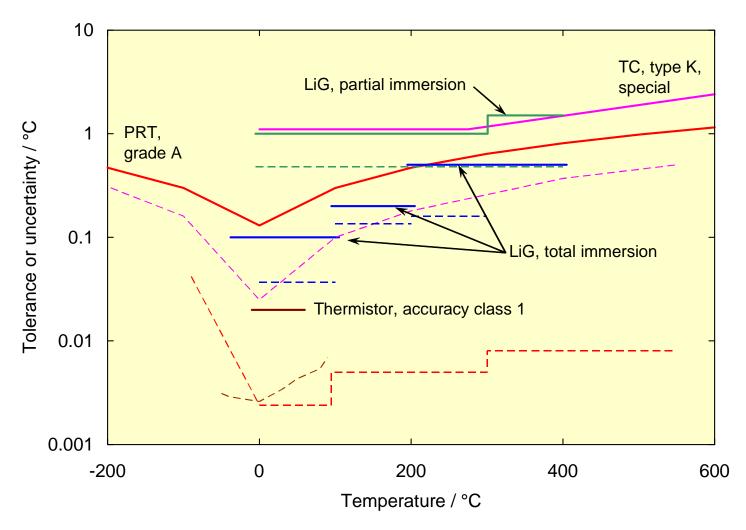
**Tolerance band:** manufacturer's guarantee that the instrument response will conform to a standard response function to within an error equal to the tolerance.

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.

### **Tolerances vs. Calibration Uncertainties**



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

Dashed lines: NIST calibration uncertainties (k=2)

### Measurement Aspects to Consider During the Transition Phase

- Measurement Bias
- Temperature Non-Uniformity
- Measurement Uncertainty
- Device Display Issues
- Non-Hg thermometers
- Validation or Re-calibration

### **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).
- 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.

### **Temperature Non-Uniformity**

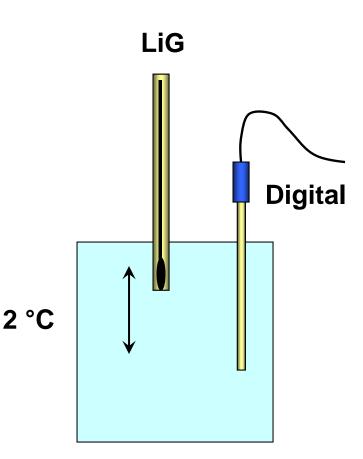
Total-Immersion Liquid-in-Glass
Thermometer: Immersion depth varies with temperature

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

Adequate immersion is often 10 times the sheath diameter

(e.g.,  $\frac{1}{4}$ " sheath = 2.5 " immersion



### Typical Measurement Uncertainty Budget: Digital Thermometer

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

Incorrect entry of calibration coefficients into readout

Probes switched without updating coefficients

Low battery

### **Consequence: Measurement cross-checks / assurance / check standards**

Routine checks of performance

Checks at ice point

Comparison of readings of different thermometers

### **EPA Activities**

# Webpages & Using Alternative Thermometers in the Field





Permission granted by the EPA

Note of thanks to Dody, EPA Chemical Engineer

### 2010: A Year in Review

#### **EPA Deliverables in FY2010**

- Web-based user-friendly guidelines
  - Replacement of Mercury Thermometers
  - Selecting Alternatives to Mercury-Filled Thermometers
  - Verification Methods to Alternatives to Mercury-Filled Thermometers, Including Research on Ice and Steam Points
  - Non-Mercury Thermometers for Validating Autoclave Operating Temperatures
  - What is Traceability?

#### Web-based videos

- Alternative Thermometers
- Ice Melting Point
- Steam Point
- Traceability



Alternatives to Hg Thermometers cc

#### Testing of alternative thermometers

- Site visit to a petroleum distribution center
- Develop field-test protocol
- Select and test alternative thermometers for accuracy and repeatability

### **Petroleum Distribution Center Thermometers**

### **4 Phase Project**

### **EPA sponsored - 2010**

- Phase I Repeatability of thermometers at NIST
- Phase II Field-testing of protocol and thermometers
- Phase III "Closing-the-Loop" Measurements at NIST





Note of thanks to those companies who donated thermometers (analog and digital) for this work

### Phase I Repeatability of Thermometers

### Petroleum Distribution Center visit to understand measurement issues

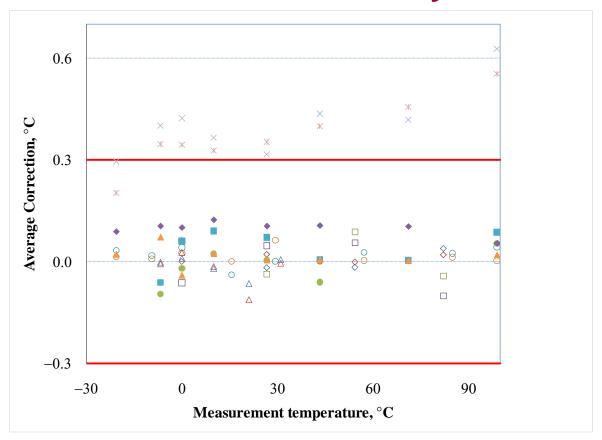
#### Thermometer selection

- ASTM Hg thermometers
  - 59F, 12F, 63F
- ASTM Organic thermometers
  - S59F
- Intrinsically-safe digital thermometers
  - 5 models

### Repeatability testing protocol performed at NIST

- Thermometers cycled through full calibration cycle 3 times
- Measurements performed by two NIST metrologists
- Temperature range of –21 °C to 99 °C

### **Phase I NIST Laboratory Results**



### One digital thermometer model did not meet the requirement of $\pm 0.3$ °C

 Manufacturer instructions used to adjust thermometers within manufacture tolerances before retesting – EASILY FIXED in lab !!!

# Phase II Field-Testing of Protocol and Thermometers

### Simple protocol developed for use at a Petroleum Distribution Center

- Based on information from exploratory trip to the Petroleum Distribution Center
  - Measurement instructions
  - Feasibility of technicians measuring several thermometers
  - Survivability of transfer standards (e.g. thermometers)
  - Data-collection worksheets

#### Five transfer standards delivered to a Petroleum Distribution Center

1 ASTM Hg with cupcase59F

1 ASTM Organic with cupcase
 S59F

3 Digitals
 DT1-3, DT1-4, DT2-1

### 8 measurements (once per week) by onsite staff

Petroleum Distribution Center reference thermometer included

### Field Testing at a Petroleum Distribution Center

### 8 measurement sets performed once per week

- 4 different technicians
- Different measurement conditions
  - Time of day / night
  - Gasoline and Ethanol
  - Weather conditions

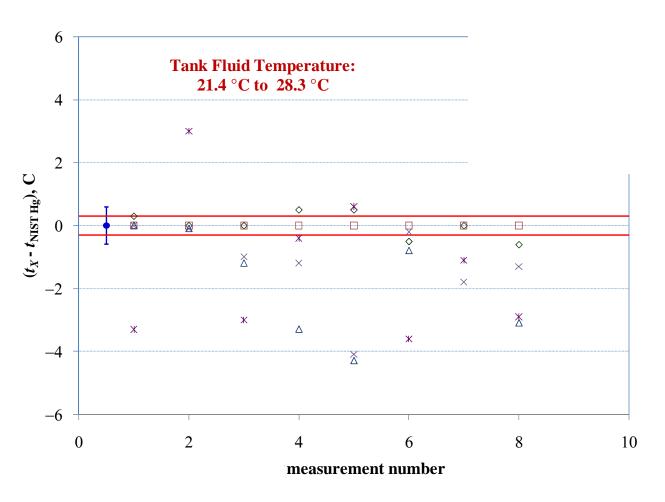
Last set performed with EPA staff, API staff, and NIST metrologists







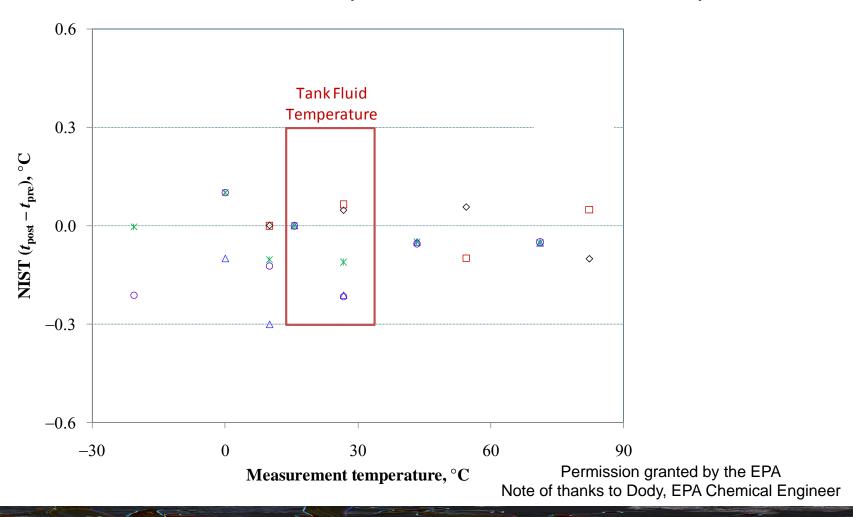
### Phase II Results in the Field



### Phase III "Closing-the-Loop" Measurements at NIST

### On return, thermometers did not significantly change

All still met ±0.3 °C requirements over tank fluid temperature



#### Phase II Notes from the Field

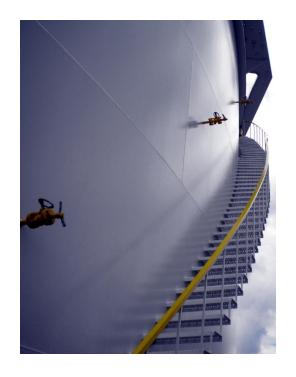
### Analog thermometer measurement resolution needs improvement

±0.6 °C resolution negatively impacts the field results

# Learning curve to overcome in using digital thermometers in the field Better Training Needed !!!

### Digital thermometer manufacturers need to work closer with Petroleum End-Users to solve various issues

- Ergonomics
- EMI
- Confidence in measurement results
- Training tutorials online videos



### **Questions?**



