2011
American Petroleum Institute
Chapter 7 Meeting

Dawn Cross

NIST

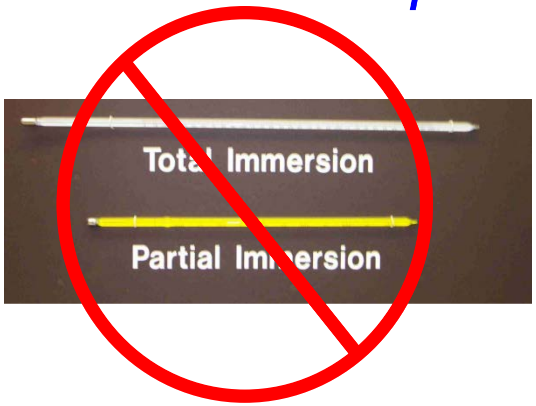
Sensor Science Division

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

PML PHYSICAL MEASUREMENT LABORATORY

Transitioning from Mercury Thermometers to Alternative Thermometers

Dawn Cross
Temperature and Humidity Group



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Global Mercury (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 Hg 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)
  - ASTM International
  - United Nations Environment Programme (UNEP) - UNEP Global Mercury Partnership
  - CDC – Centers for Disease Control and Prevention

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 mercury-in-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***

ASTM E20 Activities in Hg Thermometer Reduction

- **ASTM identified over 750 standards that require the use of Hg thermometers**
  - Through co-operative efforts, almost 500 have been changed to allow alternative thermometers to make temperature measurements
- **ASTM E20 Efforts**
  - E20.05 – Liquid-in-Glass (LiG) Thermometers and Hydrometers
  - E20.90 – Hg Reduction Initiative
  - E20.09 – Digital Contact Thermometers
    - 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…
    - Provides a number of recommendations for the manufacture and selection of a digital thermometer...

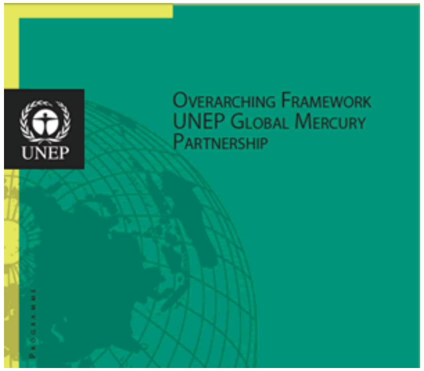
Interstate Mercury Education & Reduction Clearinghouse (IMERC)

- **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, D. Cross, and G. Strouse



Why Replace Hg Thermometers ?

- **Mercury is a neurotoxin**
    - see CDC webpages for further information www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=24
    - CDC, Agency for Toxic Substances and Disease Registry
  - 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
- **Safety Issue**
  - Cleaning up a uncontrolled Hg spill due to accidental breakage
- **To reduce Hg in the environment, several U.S. government, state agencies, and international organizations are driving the removal of Hg thermometers**

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
- **Calibration**
  - All thermometers need calibration
    - All thermometers need verification – often
    - Verification for all industrial thermometers starts with the ice melting point (0 °C)
- **Range of use**
  - Digital thermometers cover the range from at least –200 °C to 500 °C

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

What is an Industrial Platinum Resistance Thermometer (IPRT)?

2, 3, or 4-wire resistance element – nominally 100 Ω @ 0 °C

- Wire wound
- Thick film
- Thin film

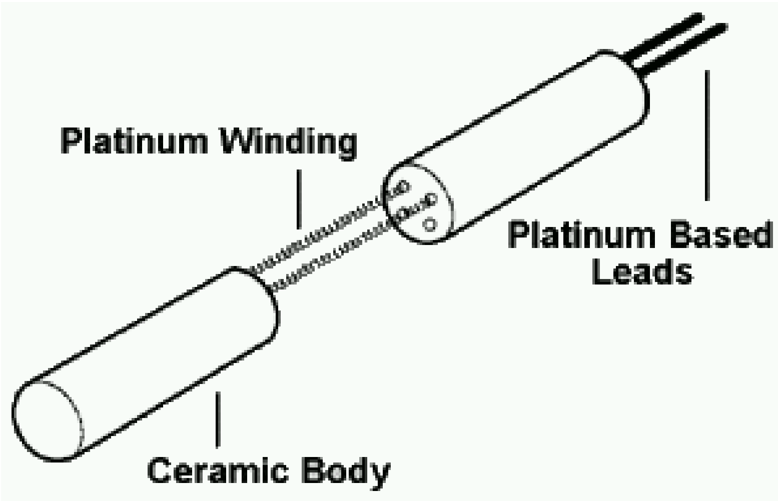
Resistance changes as a function of temperature

Positive temperature coefficient

Nominal temperature range of use:

- –200 °C to 850 °C

Nominal resistance at 0 °C

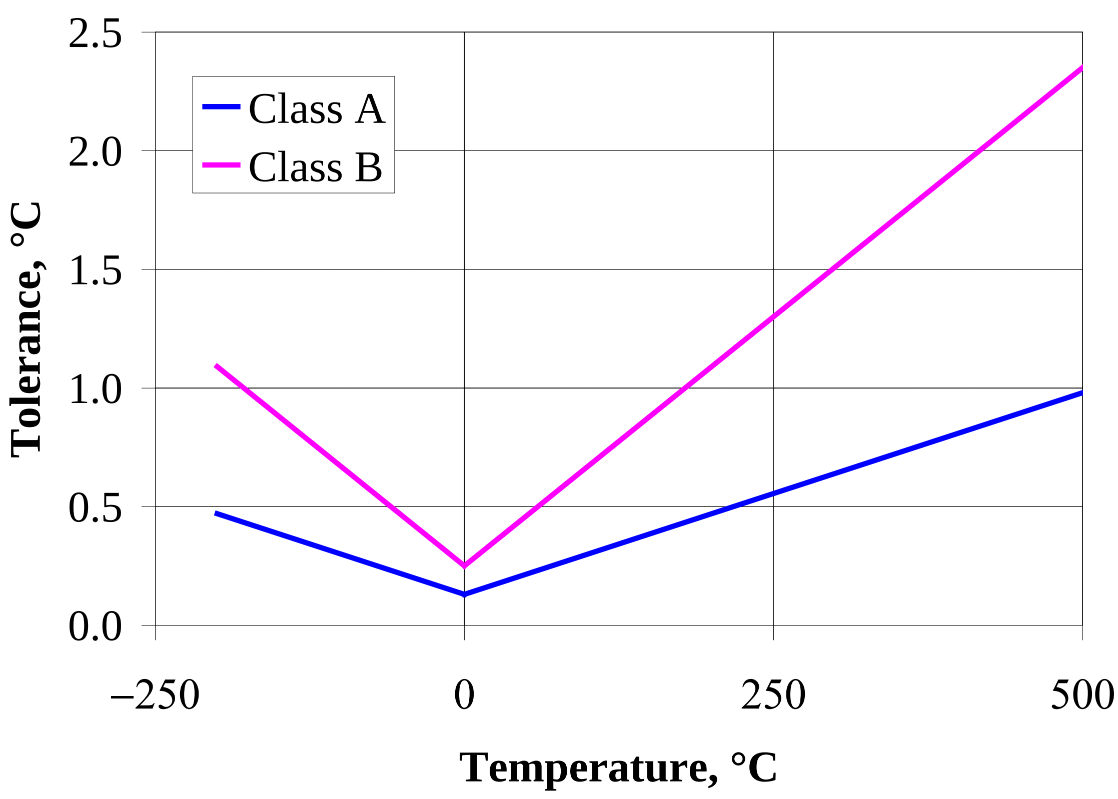


ASTM E1137 "Off the Shelf" Tolerance and Uncertainty

aka Interchangeability

Class A ±[0.13 + 0.0017 |t|] °C		
Temperature °C	Tolerance Ω	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		
Temperature °C	Tolerance Ω	Tolerance °C
–200	**0.47**	**1.1**
0	**0.10**	**0.25**
500	**0.78**	**2.4**



Considerations in Selecting IPRTs

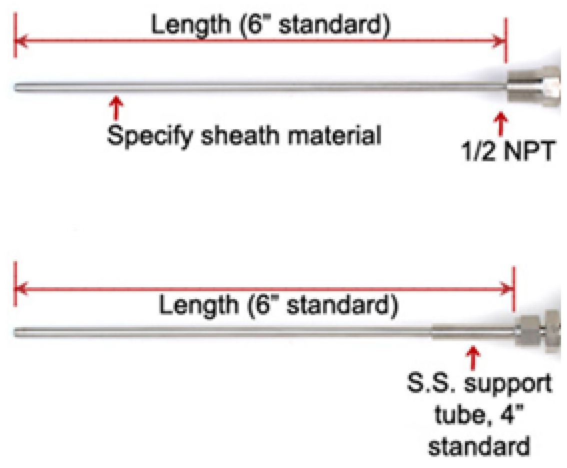
- **ADVANTAGES**
  - Wide temperature range
  - *R* vs. *T* is well characterized
  - Rugged construction
  - Readily available in different shapes and sized to meet most application requirements
  - **Can easily be used with a digital temperature read-out device**

- **DISADVANTAGES**
  - Deterioration at elevated temperatures above 500 °C
  - 2- and 3- wire devices need lead-wire compensation
  - Non-hermetically sealed IPRTs will deteriorate in environments with excessive moisture
  - **Not a defining standard of the ITS-90**

“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 – α
- 385, 390, 392

Time Response

Calibration
- “Off the Shelf” – Tolerance and Interchangeability
- Actual calibration – Lower Uncertainty

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 resolution, stability, calculation of temperature, calibration/tolerance band (interchangeability)

Multimeter

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

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

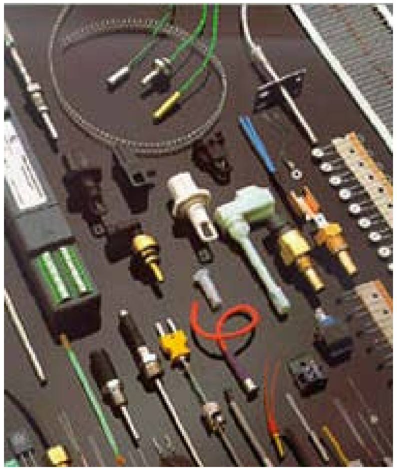
Recommendation:

- Measurement at 0 °C (Ice Melting Point) or 0.01 °C – at least
- Measurement at highest temperature of use is better

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 Ω to 100 MΩ
probe	bead in glass rod
disc	0.5 cm to 1.3 cm thick, 5 kΩ to 10 kΩ
washer	2 cm diameter
rod	moderate power capacity, 1 kΩ to 150 kΩ

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

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

Advantages and Disadvantages of Thermistors

ADVANTAGES

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 less than 0.02 °C
Interchangeable to 0.05 °C

DISADVANTAGES

Small temperature range
Needs frequent checks on calibration when exposed to t > 100 °C

Selecting a Thermocouple Type

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

type J: Common wire (Fe/CuNi) with limited temperature range

type K: Most used and accessible 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.

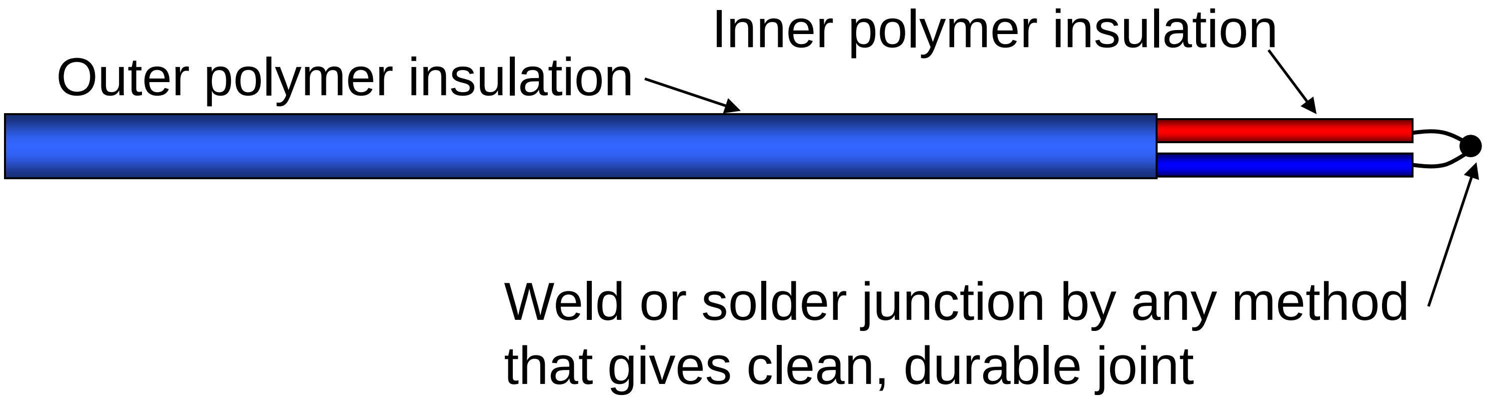
Use type R or S below 1300 °C, type B above 1300 °C.

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.

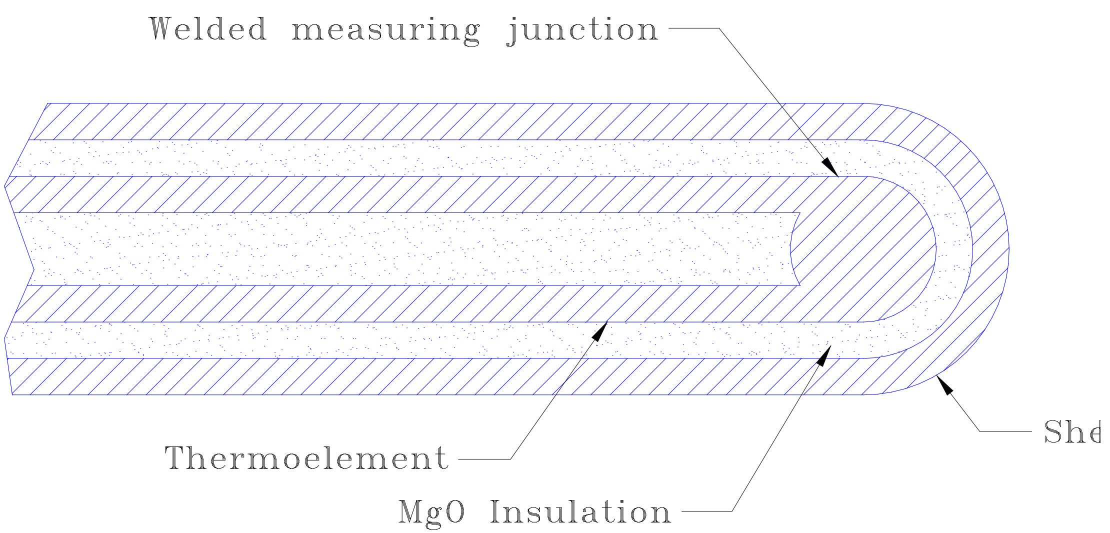
Pt/Pd: The best accuracy from 1000 °C to 1500 °C–not commercial

Soft-Insulated Thermocouples



- 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

Advantages of Thermocouples

- Readily available in different shapes and sized to meet most application requirements
- Wide temperature range (–270 °C to 2100 °C) – depends on Type (e.g., K, S)
- Small (down to 0.25 mm diameter)
- Easy to integrate into automated data systems
- Adapts easily for use as a Digital Thermometers

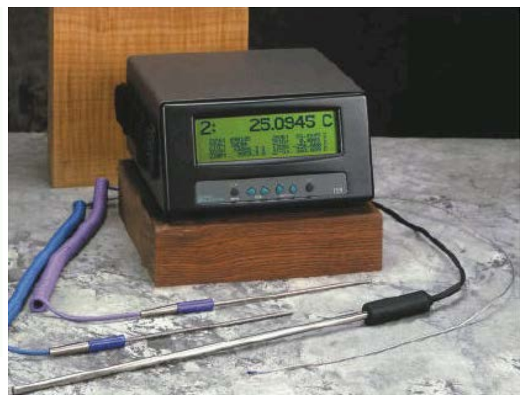
Disadvantages of Thermocouples

- 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**

- ***Measurement application, measurement uncertainty (accuracy), training in use, and maintenance are serious considerations***

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
- Hg is a powerful neurotoxin (see CDC webpages for further information)

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

Thermometers are available from many commercial sources

Calibration vs. Interchangeability (e.g., ASTM E1137 Class A Tolerance)

Temperature Range of measurement: varies by thermometer type

Stability and Durability during use

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

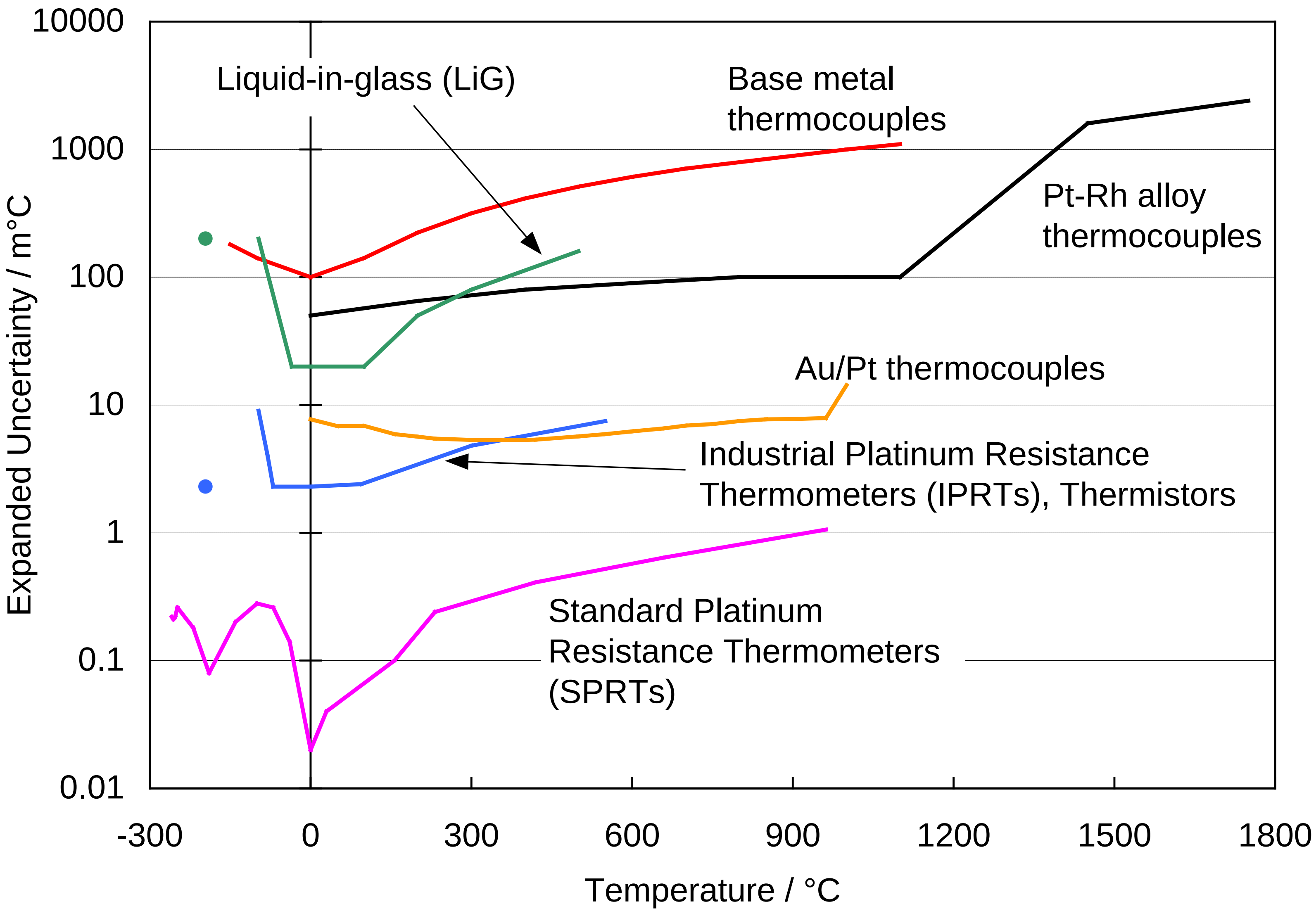
Compatibility with measurement equipment

- **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



Comparing Thermometer Types

Thermometer Type	Probe Type	ASTM	Temperature Range, °C	Calibration Method	Measurement Uncertainty, °C
Digital	IPRT	Yes	–196 to 500	Comparison	0.01 to 1
	Thermistor		–50 to 100		0.005 to 0.01
	TC		–196 to 2100		0.1 to 1
Analog	Organic LiG	Yes	–196 to 200	Comparison	1 to 3
	Proprietary LiG	Yes	–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.

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).

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.

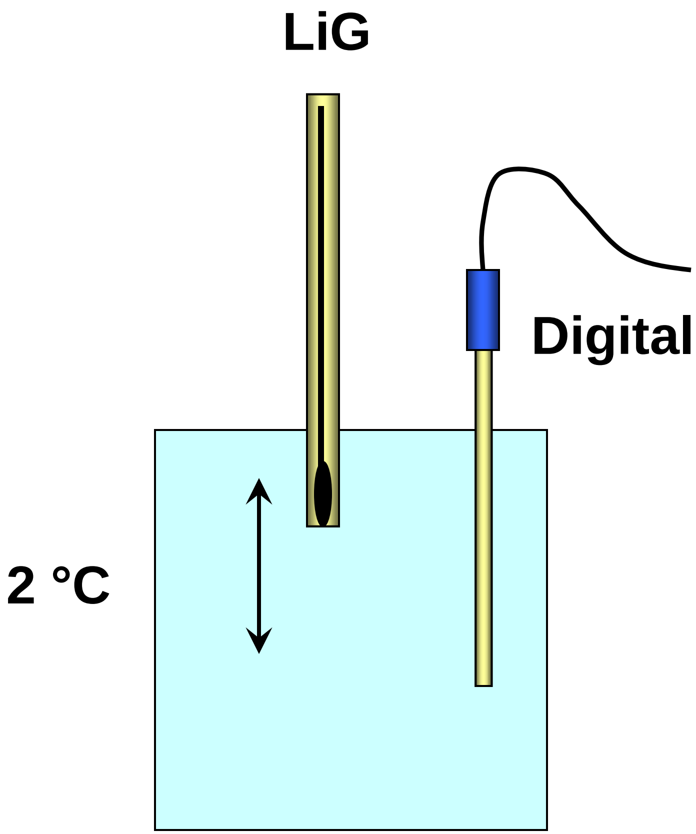
Temperature Non-Uniformity

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., ¼” 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

EPA Activities

Webpages &
Using Alternative Thermometers in the Field

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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

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Note of thanks to Dody, EPA Chemical Engineer

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

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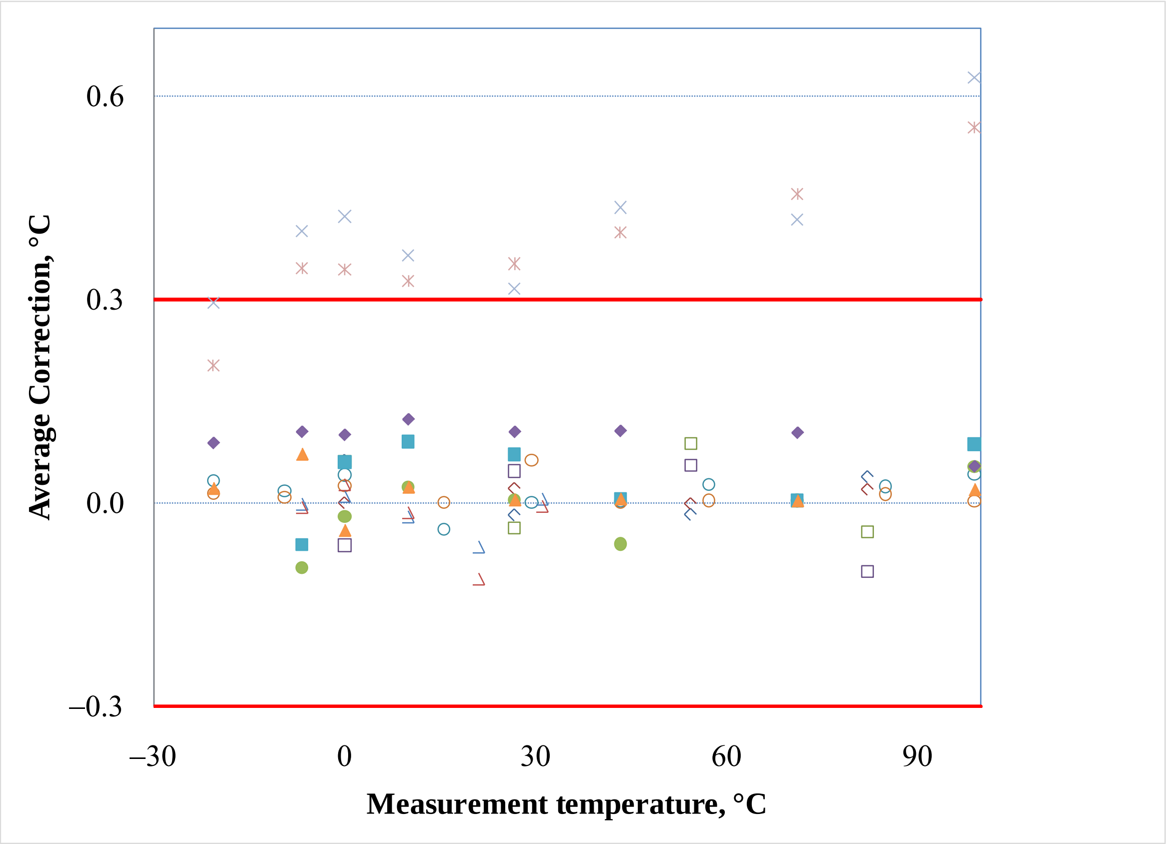
Note of thanks to Dody, EPA Chemical Engineer

Phase I NIST Laboratory Results



One digital thermometer model did not meet the requirement of ±0.3 °C

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

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Note of thanks to Dody, EPA Chemical Engineer

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 cupcase	59F
– 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

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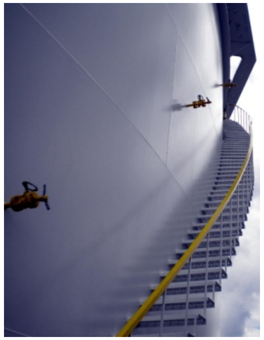
Note of thanks to Dody, EPA Chemical Engineer

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, NIST metrologists, and others



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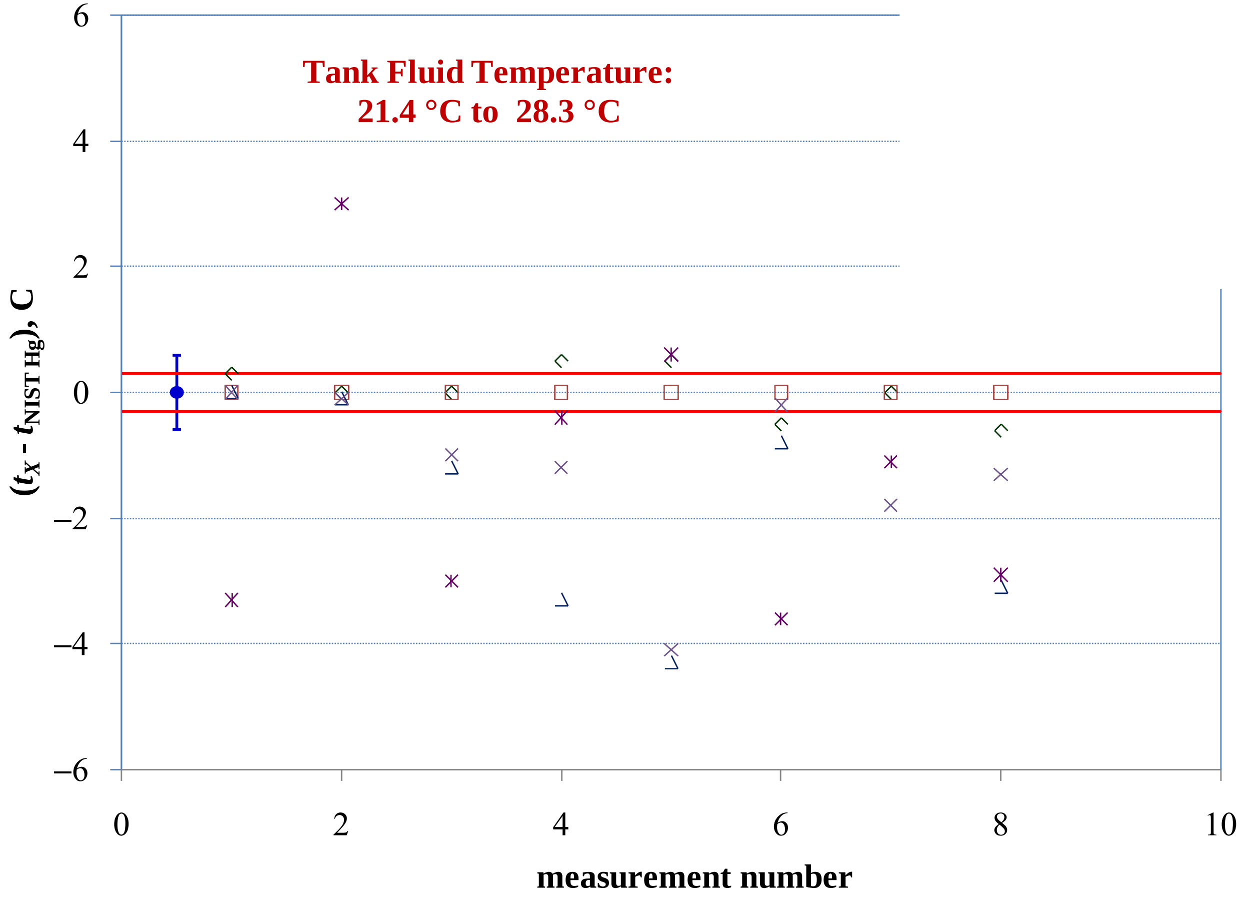
Phase II Results in the Field



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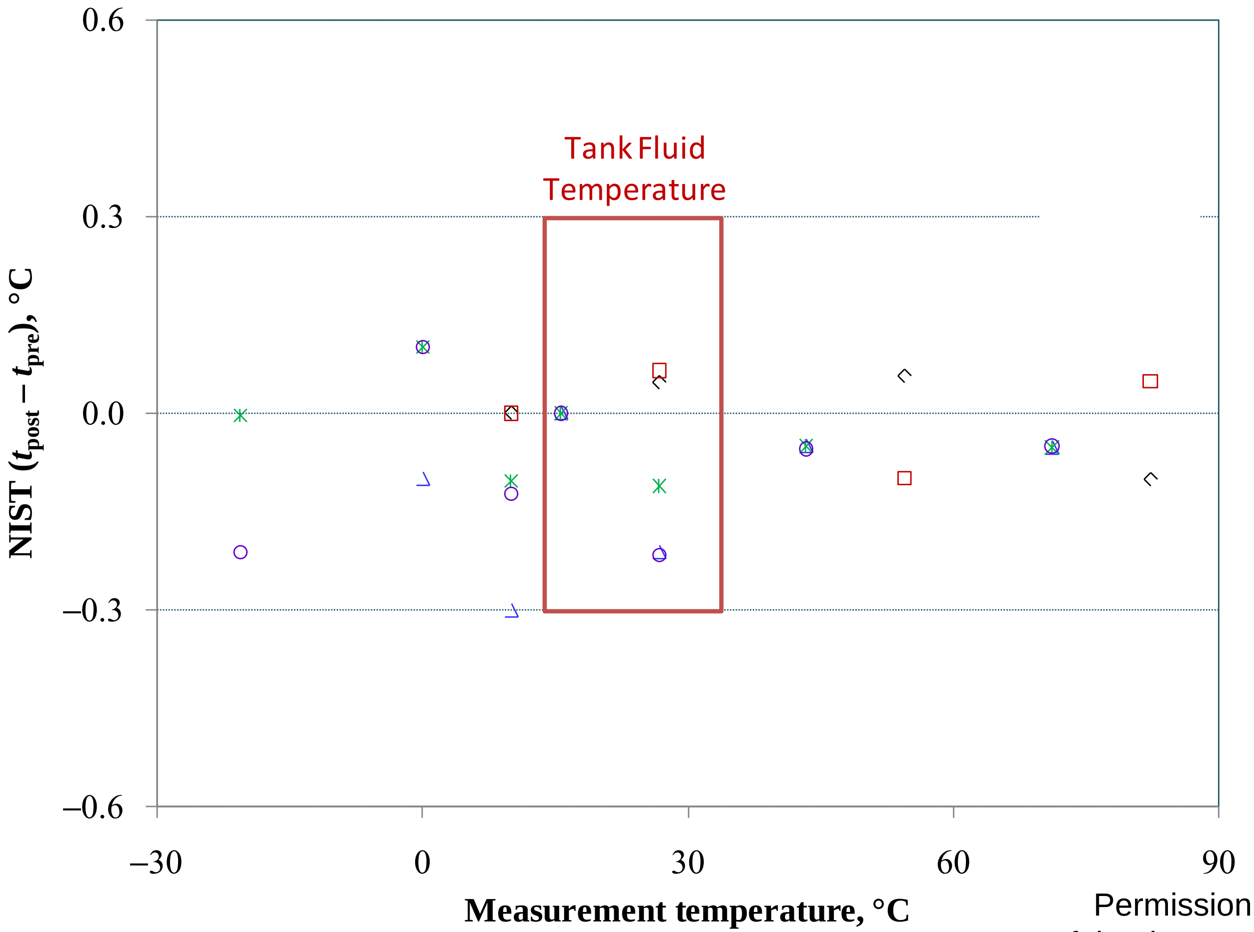
Phase III "Closing-the-Loop" Measurements at NIST

On return, thermometers did not significantly change

– ***ALL*** still met ±0.3 °C requirements over tank fluid temperature



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Phase II Notes from the Field

Analog thermometer measurement resolution needs improvement

- ±0.6 °C resolution negatively impacts the field results

NIST Educational / Informational Webpage on Alternative Thermometers - Scheduled for November 2011 -

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

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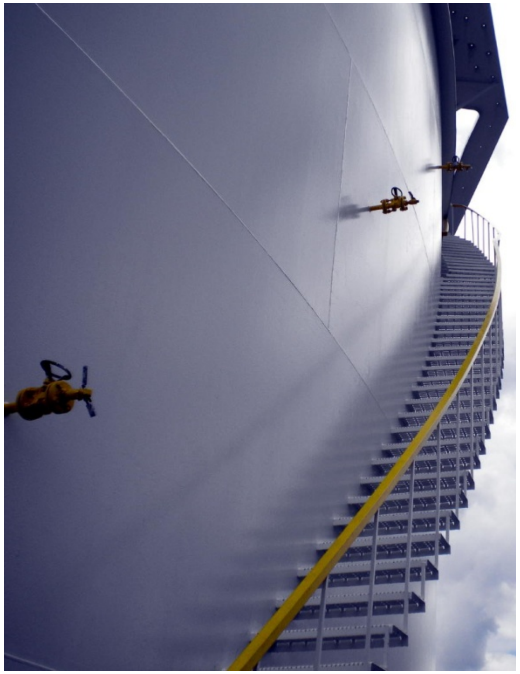

Questions ?