

# Transitioning from “Banned” Mercury Thermometers to Alternative Thermometers

## Measurement Science Conference 2013



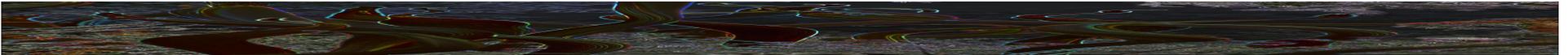
### **Technical Contacts**

Dawn Cross, 301 975 4822, [dawn.cross@nist.gov](mailto:dawn.cross@nist.gov)

Greg Strouse, 301 975 4803, [gstrouse@nist.gov](mailto:gstrouse@nist.gov)

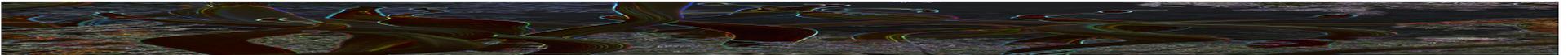
## **NIST Hg Reduction Activities**

- **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 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***
    - ***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

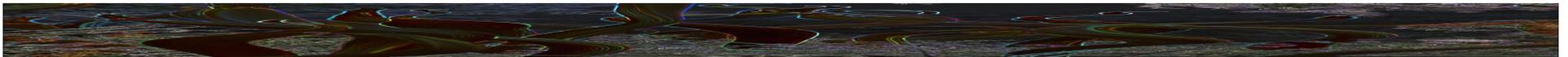
## **Organic/Proprietary Liquid-in-Glass Thermometers**

–196 °C to 200 °C

## **Digital Thermometers**

–196 °C to 550 °C

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

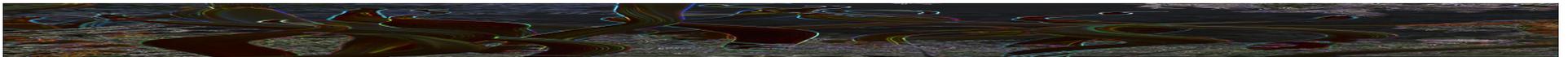


# ASTM E20 Activities in Hg Thermometer Reduction

- **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.

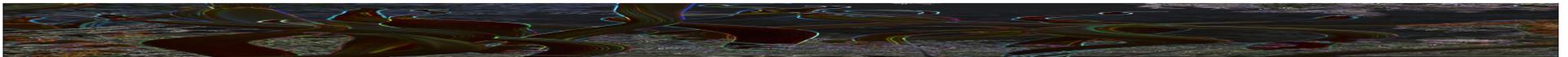
### ➤ The IMERC state members include

- 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)

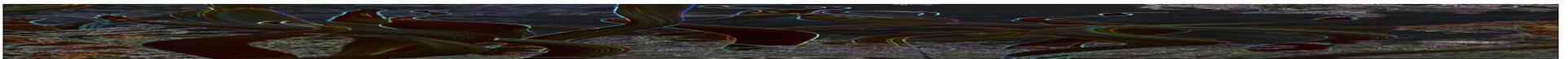
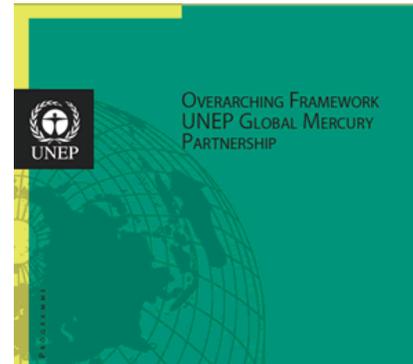
- **Cannot sell, offer for sale, or distribute mercury-added thermometers if a non-mercury alternative is available**; excludes mercury-added thermometers that are a component of a larger product in use prior to January 1, 2008 or resale manufactured before January 1, 2008; excludes if the use is a federal 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 D. Cross



# 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.**



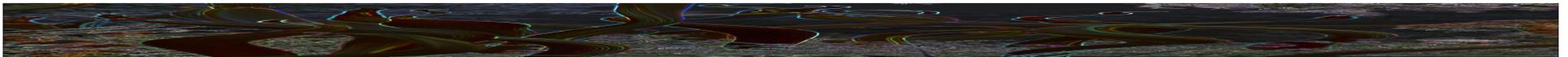
# Measurement Truths to Consider

- **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  $-200\text{ }^{\circ}\text{C}$  to  $500\text{ }^{\circ}$



# 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

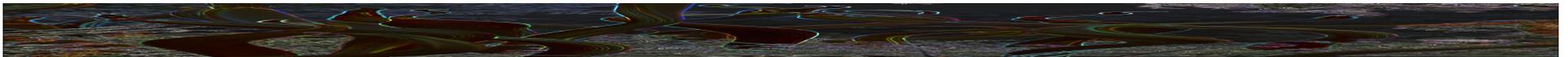
#### > Thermocouples

–196 °C to 2100 °C



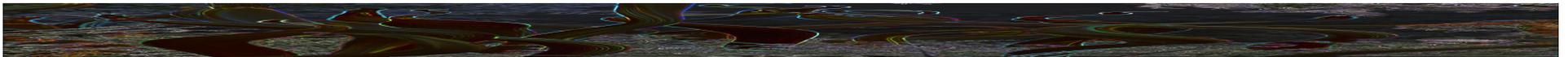
# Digital Thermometers

- **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



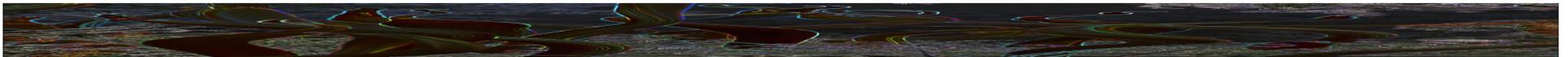
# Choice of a LiG Thermometer

## Advantages of LiG thermometers

- Relatively inexpensive
- When used at moderate temperatures ( $<150\text{ }^{\circ}\text{C}$ ), 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**

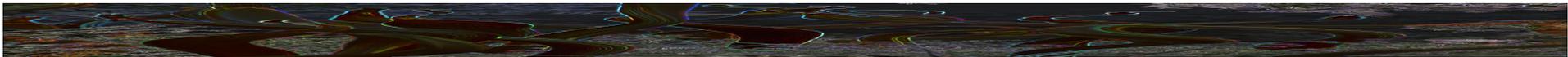
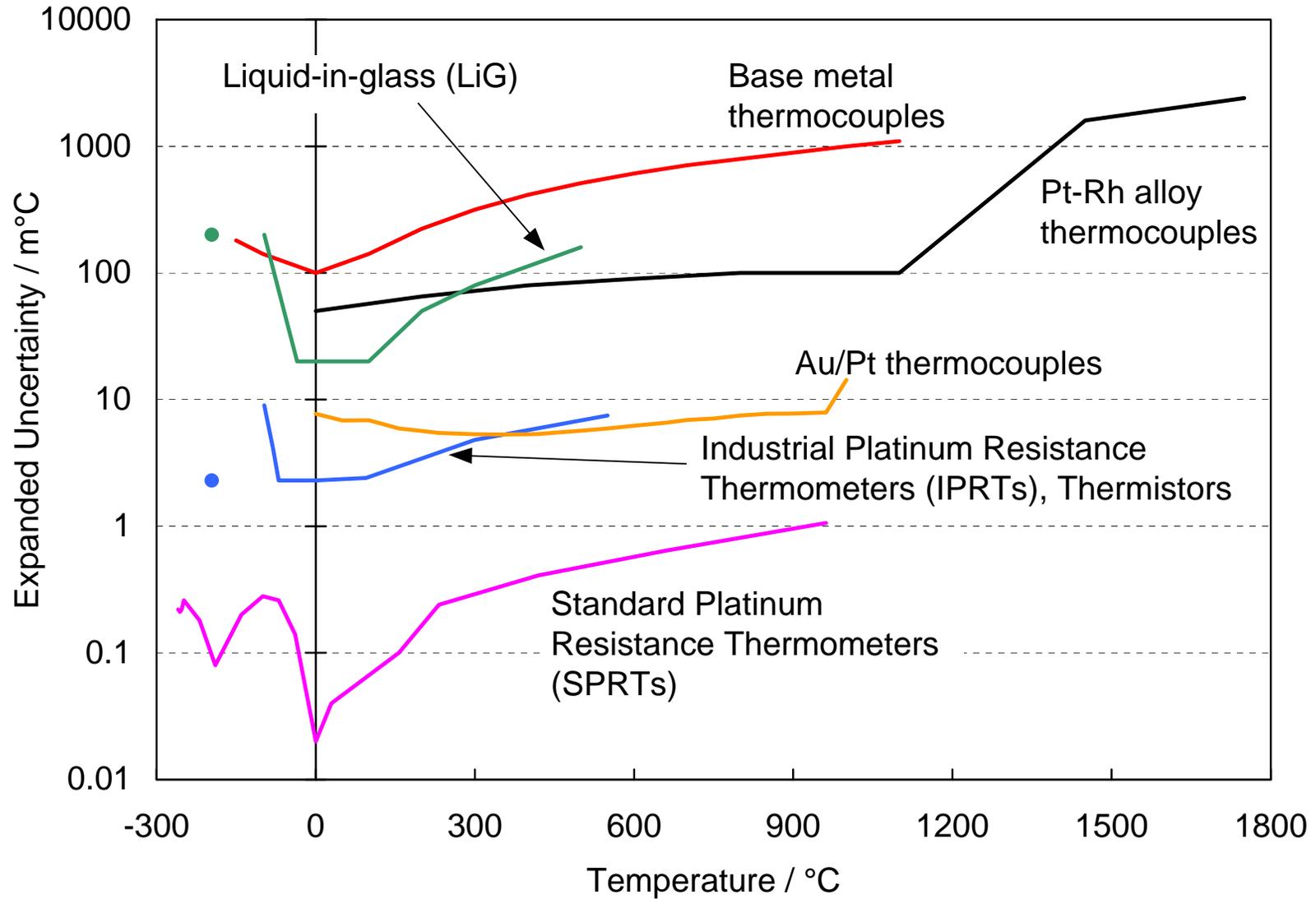
- Digital probes easy to integrate to electronics
- liquid-in-glass, digital thermometers much easier for quick visual inspection

**Compatibility with object being measured**

- sheath diameter, length chosen for good thermal equilibrium

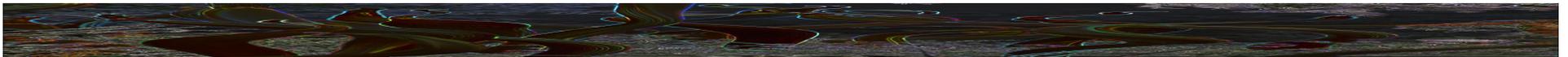


# Thermometer Types: Calibration Ranges and Uncertainties



## Comparative Thermometer Types: Calibration Methods, Uncertainties, and Costs

Thermometer Type	Probe Type	Nominal Cost, \$	Temperature Range, °C	Calibration Method	Measurement Uncertainty, °C
<b>Digital</b>	IPRT	5 to 1,000	-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
<b>Analog</b>	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.

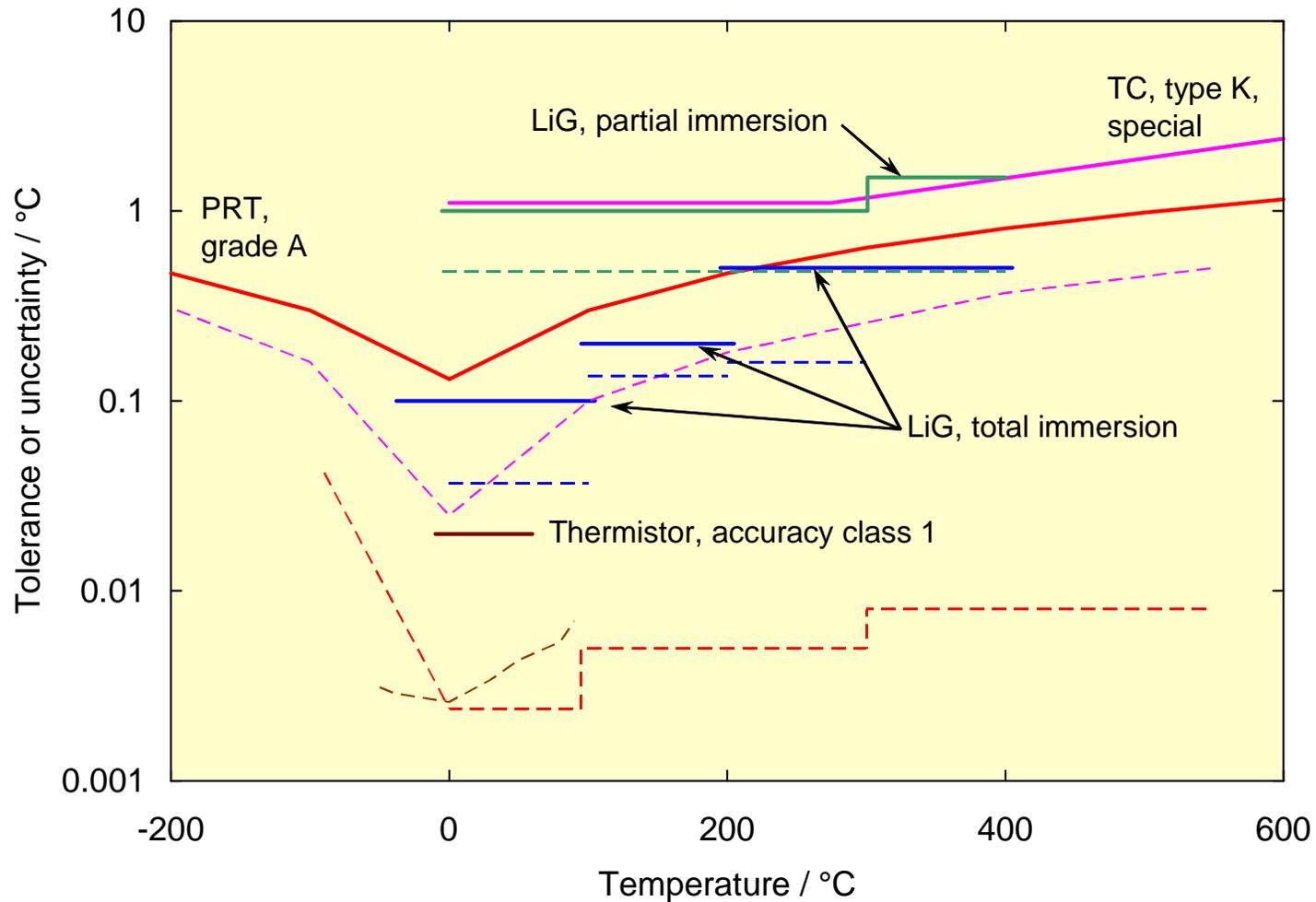
**Calibrated thermometer:** may or may not have a response close to the nominal response function for that thermometer type.

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



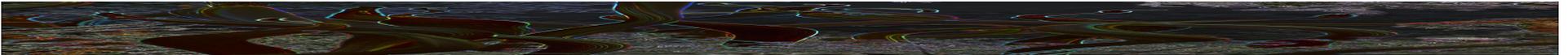
Colored lines: ASTM tolerances (ASTM E1, E1137, E230, and E879).

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



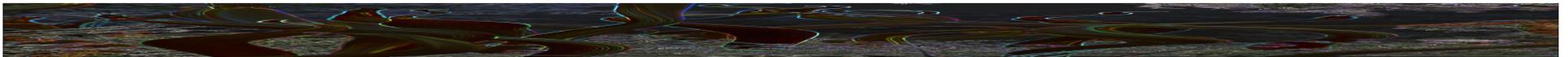
## **Measurement Aspects to Consider During the Transition Phase**

- **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).
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

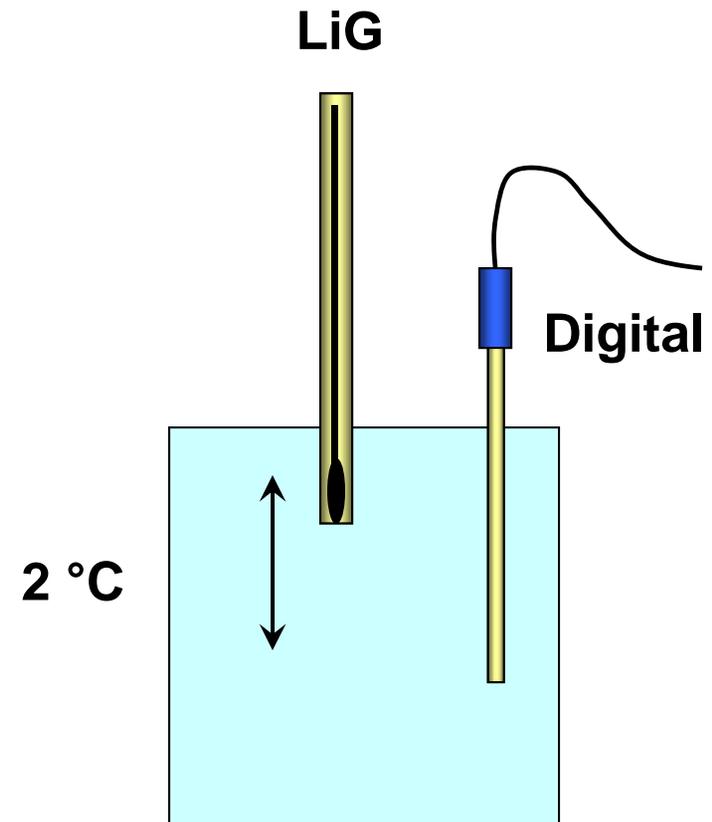
## Partial-Immersion Liquid-in-Glass

**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

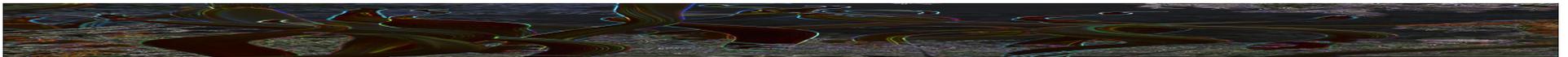
(e.g.,  $\frac{1}{4}$ " sheath = 2.5 " immersion)



## Typical Measurement Uncertainty Budget: Digital Thermometer

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

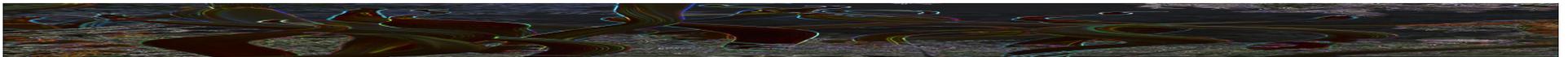
Low battery

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

Routine checks of performance

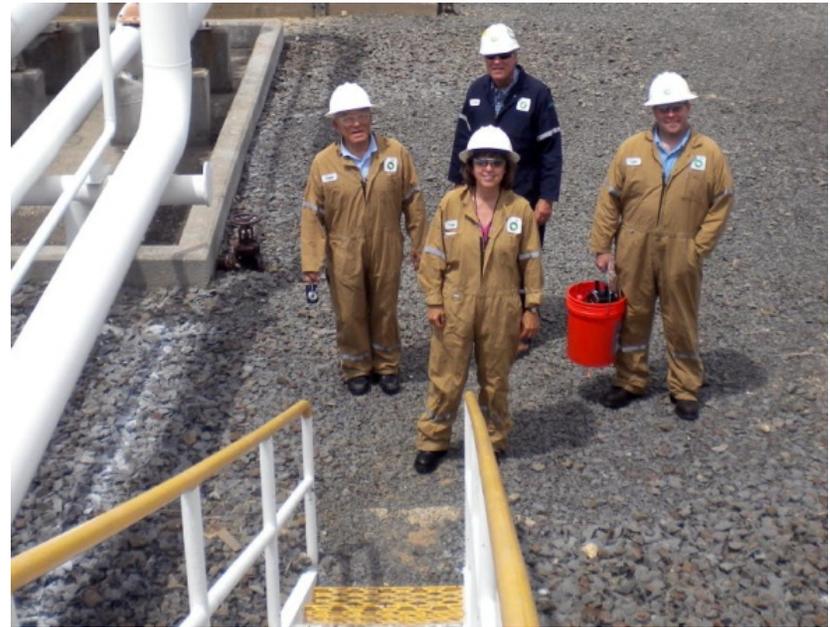
Checks at ice point

Comparison of readings of different thermometers



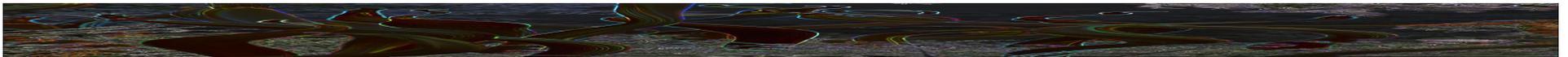
# EPA Activities

## Webpages & Using Alternative Thermometers in the Field



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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

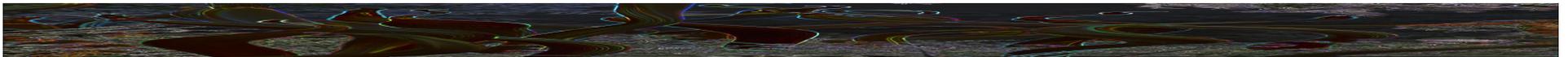


Alternatives to Hg Thermometers 

### – 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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# Petroleum Distribution Center Thermometers

## 4 Phase Project

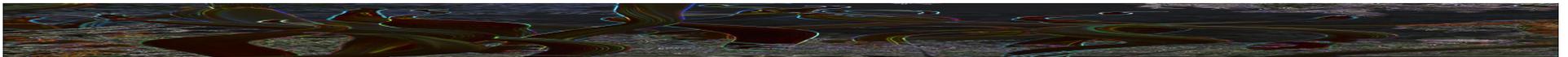
### EPA sponsored - 2010

- 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

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# Phase I

## Repeatability of Thermometers

**Petroleum Distribution Center visit to understand measurement issues**

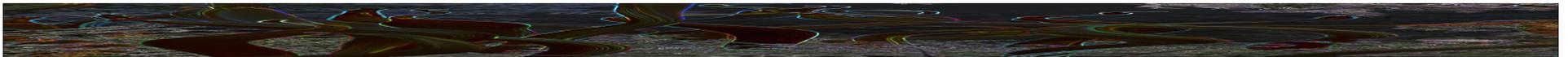
### **Thermometer selection**

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

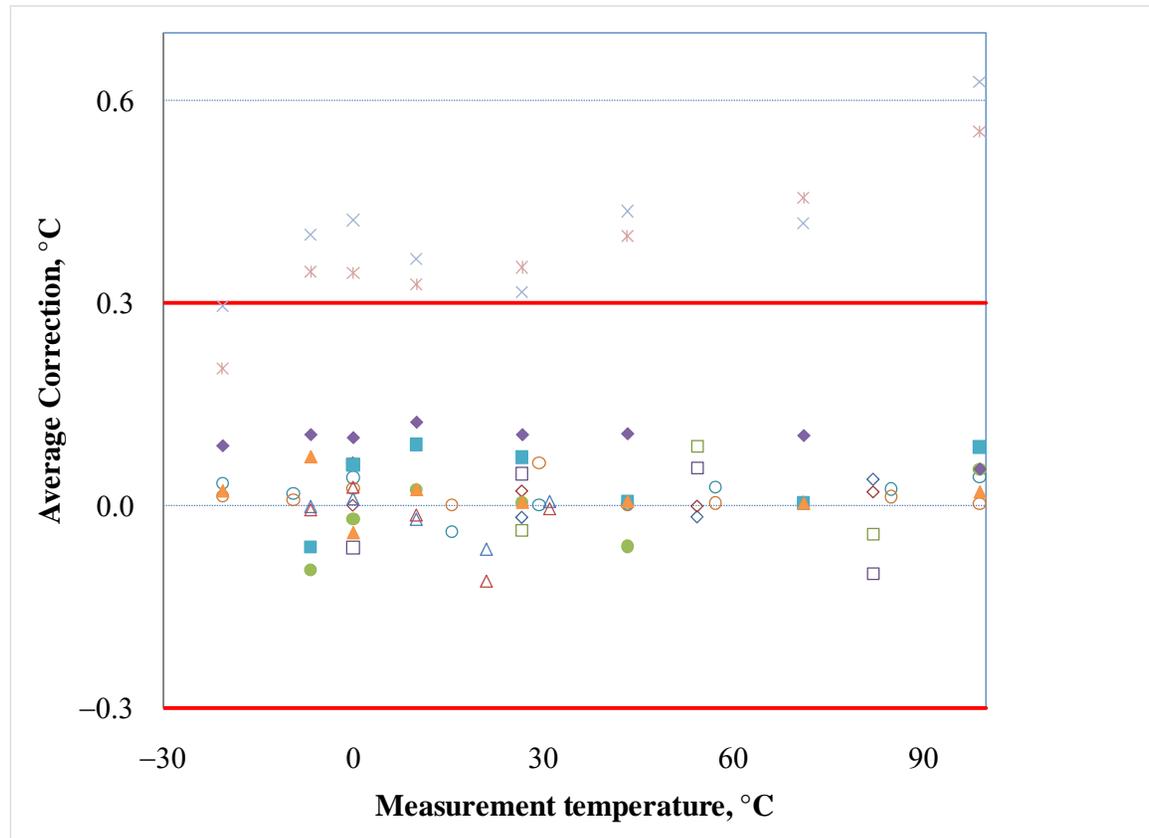
### **Repeatability testing protocol performed at NIST**

- Thermometers cycled through full calibration cycle 3 times
- Measurements performed by two NIST metrologists
- Temperature range of  $-21\text{ }^{\circ}\text{C}$  to  $99\text{ }^{\circ}\text{C}$

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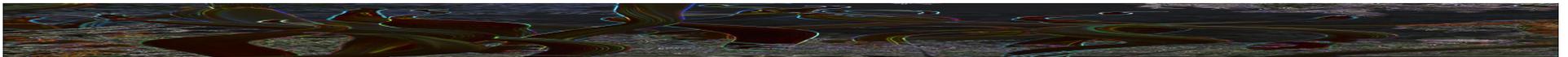
# Phase I NIST Laboratory Results



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 !!!**

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## **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

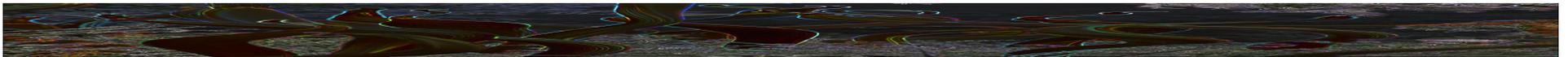
#### **Five transfer standards delivered to a Petroleum Distribution Center**

- 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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# Field Testing at a Petroleum Distribution Center

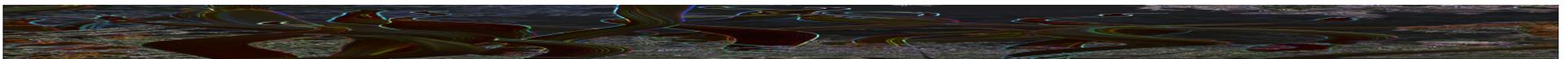
## 8 measurement sets performed once per week

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

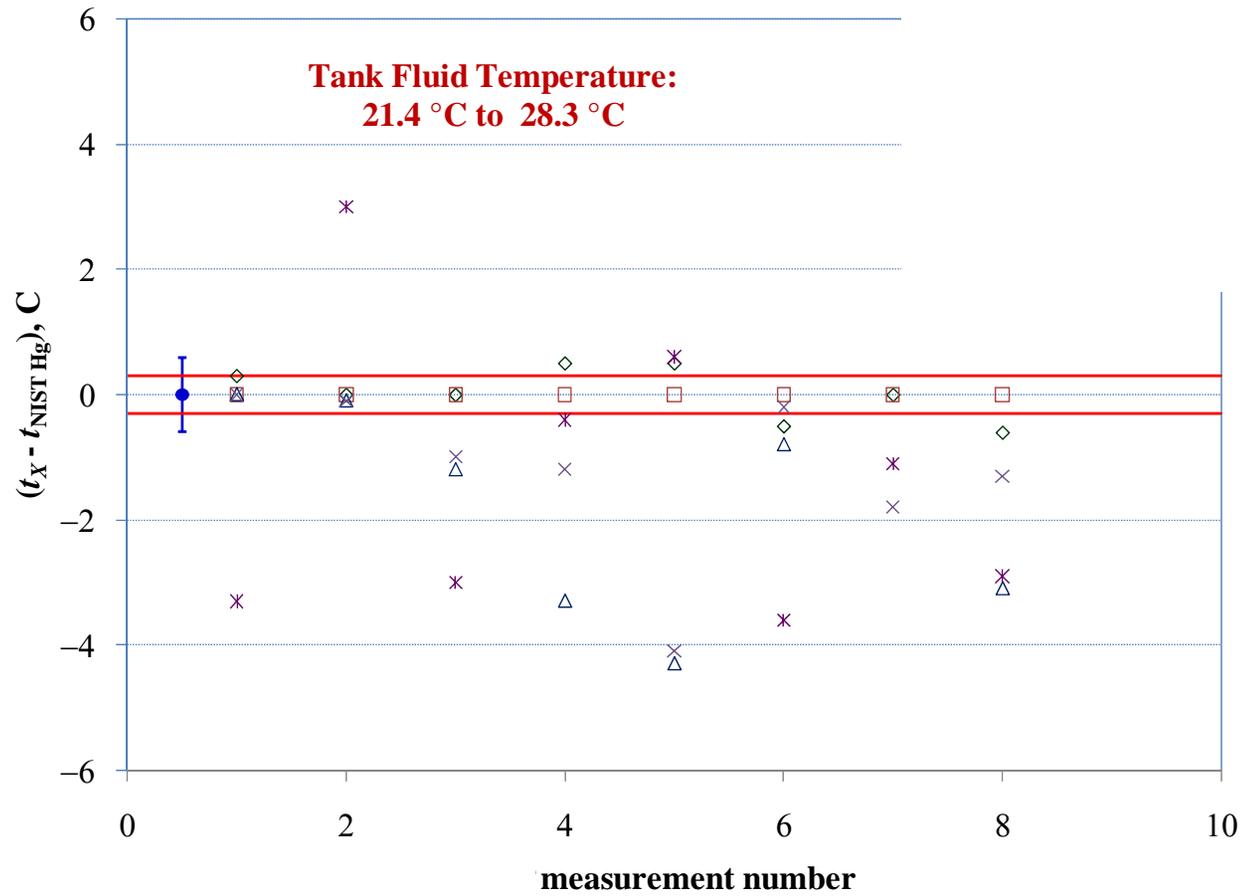
Last set performed with EPA staff,  
API staff, and NIST metrologists



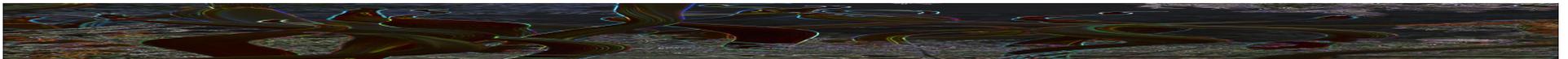
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# Phase II Results in the Field



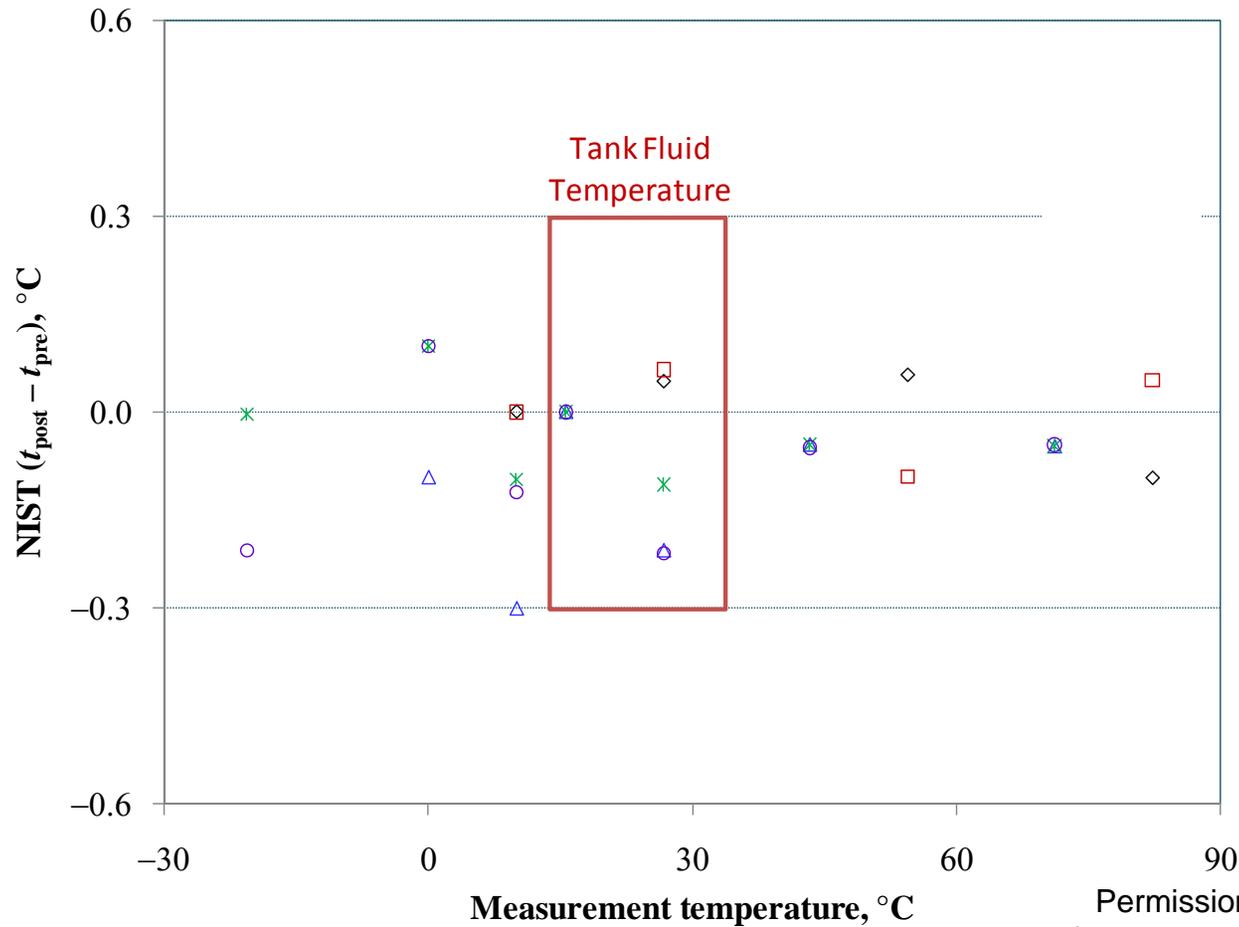
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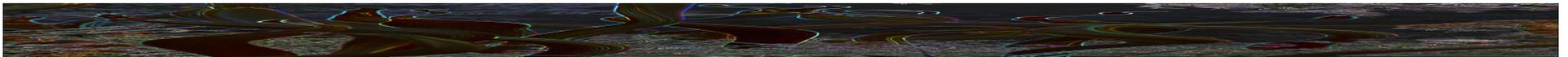
# Phase III “Closing-the-Loop” Measurements at NIST

On return, thermometers did not significantly change

- All still met  $\pm 0.3$  °C requirements over tank fluid temperature



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## Phase II Notes from the Field

**Analog thermometer measurement resolution needs improvement**

- $\pm 0.6$  °C resolution negatively impacts the field results

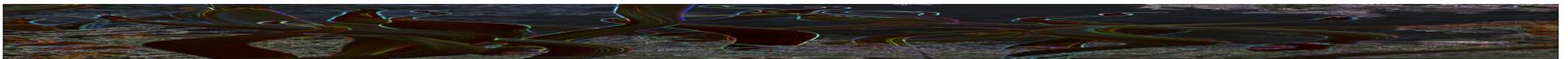
**Learning curve to overcome in using digital thermometers in the field**

**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

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# Questions ?

