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Replacing “Banned” Mercury-in-Glass Thermometers

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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:

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

Expanded Uncertainty / m°C

Liquid-in-glass (LiG)  Base metal thermocouples
Pt-Rh alloy thermocouples
Au/Pt thermocouples
Industrial Platinum Resistance Thermometers (IPRTs), Thermistors
Standard Platinum Resistance Thermometers (SPRTs)
### Comparative Thermometer Types: Calibration Methods, Uncertainties, and Costs

<table>
<thead>
<tr>
<th>Thermometer Type</th>
<th>Nominal Cost, $</th>
<th>Temperature Range, °C</th>
<th>Calibration Method</th>
<th>Calibration $U (k=2)$, °C</th>
<th>Calibration Cost, $</th>
</tr>
</thead>
<tbody>
<tr>
<td>Digital Thermometer</td>
<td>Uncertainty Driven 50 to 25,000</td>
<td>Depends on Need</td>
<td>System or Separate?</td>
<td>Depends on How Used</td>
<td>1000</td>
</tr>
<tr>
<td>IPRT</td>
<td>100 to 1000</td>
<td>–196 to 500</td>
<td>Comparison</td>
<td>&lt;0.01</td>
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</tr>
<tr>
<td>Thermistor</td>
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</tr>
<tr>
<td>Thermocouple, Noble Metal</td>
<td>600</td>
<td>0 to 1100</td>
<td>Comparison</td>
<td>0.3</td>
<td>1000</td>
</tr>
<tr>
<td>Thermocouple, Base Metal</td>
<td>6 to 50</td>
<td>0 to 1100</td>
<td>Comparison</td>
<td>1</td>
<td>1000</td>
</tr>
<tr>
<td>Organic LiG</td>
<td>30</td>
<td>–196 to 200</td>
<td>Comparison</td>
<td>&lt;2</td>
<td>1000</td>
</tr>
</tbody>
</table>
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**

<table>
<thead>
<tr>
<th>Component</th>
<th>Method of evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration uncertainty or tolerance</td>
<td>Manufacturer or calibration laboratory, or ASTM E 230 tolerance</td>
</tr>
<tr>
<td><strong>Thermocouple drift</strong></td>
<td>Results from literature, or in situ comparisons</td>
</tr>
<tr>
<td>Reference junction uncertainty</td>
<td>Manufacturer or independent evaluation</td>
</tr>
<tr>
<td><strong>Readout uncertainty</strong></td>
<td>Manufacturer or independent evaluation</td>
</tr>
<tr>
<td><strong>Readout drift</strong></td>
<td>Manufacturer or independent evaluation</td>
</tr>
</tbody>
</table>

*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.
**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 to 1400 °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:
  - \(-200 \, ^\circ C \text{ to } 850 \, ^\circ C\)
- Nominal resistance at 0 \(^\circ C\)
  - \(100 \, \Omega\)

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

Where is the probe inserted?
- Stirred-liquid baths give excellent heat transfer
- A stagnant air gap has poor heat transfer

Sensor length can vary from 4 mm to 30 mm
- 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.
- 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

![Graph](image)
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.