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Selection of Alternatives to Liquid-in-Glass Thermometers

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Abstract: A desire to increase automation or to eliminate the use of mercury has prompted several ASTM committees to consider alternatives to ASTM Liquid-in-Glass (LiG) thermometers. In this paper, we address the technical issues of choosing an alternative. We first discuss the basic properties and relative merits of platinum resistance thermometers, thermistors, and thermocouples in the context of replacements for LiG thermometers; then list uncertainty components for measurements with alternative thermometers; and finally discuss other factors in temperature measurement and control that are important in the development and execution of ASTM standards.

Keywords: liquid in glass, mercury, resistance thermometer, temperature, thermistor, thermocouple, thermometer, temperature

Introduction

Many hundreds of ASTM test methods rely on ASTM liquid-in-glass (LiG) thermometers defined in ASTM Specification for ASTM Liquid-in-Glass Thermometers (E 1) or ASTM Liquid-in-Glass Thermometers with Low-Hazard Precision Liquid (E 2251). Some ASTM committees are now discussing whether other types of thermometers, such as platinum resistance thermometers (PRTs), thermistors, or thermocouples, may be included as alternatives in a number of standards. In this document, we describe the technical issues relevant to the specification of alternative thermometer types, in order to serve as a guide to re-evaluation of thermometry requirements in ASTM standards.

Prior to selection of an alternative thermometer, the application requirements must be reviewed. In particular, the measurement uncertainty, temperature range, and operating environment should be established.

Properties of Thermometer Types

Liquid-in-Glass thermometers

Liquid-in-glass thermometers consist of a liquid, such as mercury or petroleum distillates, enclosed in a glass bulb that has a graduated capillary extending from the bulb. Because the liquid has a larger coefficient of thermal expansion than the glass, the liquid rises in the capillary upon heating.

Variations in thermometer design are necessary to obtain optimal performance. Total immersion thermometers, which require immersion in the test medium almost to the top of the liquid column in the capillary, are the most accurate but require physical adjustment of the depth of thermometer immersion with each change in temperature. Partial immersion thermometers, which are set to a fixed immersion, are more convenient but have greater errors due to uncertainties of the temperature of the liquid column. Additionally, the range of the thermometer is a balance between desired resolution for the thermometer and a large usable range of temperatures.

The liquid-in-glass thermometers of ASTM E 1 and E 2251 are designed to meet the tolerance described as “Scale error, max” in Tables 1 of ASTM E 1 and E 2251 for extended periods of usage. A tolerance specifies the maximum error between the thermometer reading and the true temperature, either in typical usage or under conditions of use specified by the appropriate standard. In contrast, the term “uncertainty” is used to describe the statistically likely range of a measurement relative to the true temperature. A quick scan of instrumentation catalogs will uncover a number of PRTs or thermistors with initial tolerances less than the maximum scale error of a liquid-in-glass thermometer. However, the initial tolerances or calibration uncertainties of PRTs, thermistors, and thermocouples do not adequately describe the total uncertainty in use, and care must be taken to account for all components of uncertainty in use when specifying an alternative to an ASTM E 1 or E 2251 thermometer.

Potential advantages of PRTs, thermistors, or thermocouples over LiG thermometers are possibly smaller uncertainties, the ease of automation, the independence of the reading from the visual judgment of the user, and the absence of mercury, which is used as the thermometric liquid in many of the ASTM E 1 thermometers. Disadvantages of these alternatives to LiG thermometers are the need for a power source for the readout and somewhat higher initial cost. Additionally, LiG thermometers, at least when used at temperatures below 150 °C or so, require only a single-point recalibration at the ice point. PRTs and thermistors generally require a minimum of three points for a recalibration, although a two-point check at the lowest and highest temperatures of use may validate an existing calibration. An ice point bath, consisting of finely divided ice and distilled water, is a highly reproducible calibration point at 0 °C that can be produced with simple equipment, as described in Ref. [1] and ASTM Practice for Preparation and Use of an Ice-Point Bath as a Reference Temperature (E 563). An additional advantage of LiG thermometers unique to applications in ASTM standards is that many of the ASTM E 1 thermometers are specially designed for use with specific ASTM tests. In these cases, the LiG thermometer may be optimized in range and resolution for a particular test, and a LiG thermometer may be a very cost-effective means of accurately determining the temperature.

In some cases, the only disadvantage to a LiG thermometer may be its use of mercury as the thermometric liquid. In this case, organic-liquid-filled thermometers specified in E 1 may be an alternative for applications with low accuracy requirements, or the LiG thermometers specified in ASTM E 2251 may be used for higher accuracy requirements.

Platinum Resistance Thermometers and Thermistors

Platinum resistance thermometers (PRTs) and thermistors both rely on the known variation of electrical resistance with temperature of a specially constructed resistor to convert temperature into a measurable electrical property. We distinguish between the *sensor*, which is the resistor and often an electrical insulator that supports the resistor, from a *thermometer*, which consists of the sensor, lead wires, and generally a protective sheath.

Thermistors have stabilities approaching a few thousandths of a degree Celsius per year when properly constructed and are highly sensitive (approximately 4 % change in resistance per degree Celsius). However the usable temperature range is limited to not more than 100 °C for a single thermistor, and the approximate maximum temperature of use is 110 °C. Near this temperature and above, the rate of sensor drift may be relatively high compared to drift near room temperature. The best stability is obtained with thermistors coated or encapsulated in glass [2]; epoxy-coated thermistors are susceptible to water absorption and subsequent drift. Thermistors are an attractive alternative to LiG thermometers when the application is close to room temperature. A number of standardized designs are described in ASTM Specification for Thermistor Sensors for Clinical Laboratory Temperature Measurement (E 879), and these designs are suitable for general purpose use, as well as uses in clinical laboratories.

Platinum resistors have a substantially wider operating range compared to thermistors, but they have a sensitivity 10 times smaller (approximately 0.4 % change in resistance per degree Celsius). Performance of a platinum resistance thermometer is highly dependent on the construction of the sensing element. Standard Platinum Resistance Thermometers (SPRTs) [4] are the most accurate thermometers available (with uncertainties of the order of 0.001 °C), but the delicacy of the strain-free resistance element of an SPRT makes it unsuitable as an alternative for most LiG thermometers. In contrast, PRT elements constructed from platinum wires that are supported in some manner or constructed from thin or thick films of platinum, have much more resistance to shock but also display significant hysteresis when used over a wide temperature range—that is, the sensor resistance at a single temperature will vary depending on the past thermal cycling of the sensor element. For any given uncertainty requirement, a PRT with sufficiently low hysteresis can be found, but at the cost of reduced ruggedness. Special designs that use a substrate with a thermal expansion coefficient close to that of the platinum sensing resistor may be robust and still offer low hysteresis. In general, PRTs are a good alternative to liquid-in-glass thermometers for applications that require temperature measurements outside the useful range of thermistors. ASTM Specification for Industrial Platinum Resistance Thermometers (E 1137) provides a full specification for PRTs appropriate for use as replacements for LiG thermometers.

Readouts for platinum resistance thermometers and thermistors may be AC bridges, or DC ohmmeters or multimeters. Specialized readouts that display results in units of temperature are based on either an AC bridge or DC ohmmeter and use software to convert the resistance value to units of temperature. For PRTs, readouts displaying temperature units commonly implement the response curves specified in E 1137, which are identical to those in the international standard [5]. Use of a thermistor response curve with a readout displaying temperature units typically requires entry of coefficients. For the highest accuracies, especially for platinum resistance thermometers, a four-wire resistance measurement is necessary.

For both thermistors and PRTs, periodic measurements at the ice point are a useful check for drift in the sensor. However, unlike LiG thermometers, the instrument response cannot be reliably adjusted using an ice-point measurement alone. At a minimum, a check at the high and low ends of the range of usage is necessary.

Considering these factors, the relevant components of uncertainty for a temperature measurement performed with a PRT or thermistor are described in Table 1. For industrial-grade PRTs, drift, hysteresis, and self-heating are highly dependent on details of the sensor design and construction. As a result, information from the manufacturer or independent evaluation is preferred over values obtained from the scientific literature for these components in particular.

Table 1. Uncertainty components for temperature measurement with a PRT or thermistor.

Component	Method of evaluation
Calibration uncertainty or tolerance	Manufacturer, calibration laboratory, or ASTM tolerance
Sensor drift	Manufacturer's specifications, or user history
Hysteresis of alternative sensor (PRTs only)	ASTM Test Methods for Testing Industrial Resistance Thermometers (E 644), implemented by manufacturer or user
Self-heating	Manufacturer or independent evaluation
Readout uncertainty	Manufacturer or independent evaluation
Readout drift	Manufacturer or independent evaluation

Thermocouples

Thermocouples (TCs) consist of two lengths of dissimilar metals, joined at one end to form a measuring junction. Each length, referred to as a thermoelement, develops a voltage (or more accurately a thermoelectric electromotive force) along its length wherever the thermoelement passes through a temperature gradient.

Typically, a voltmeter is connected to the ends of the thermoelements opposite the measuring junction, and the net difference between the voltages created by the two thermoelements is measured. The connections of the thermoelements to the voltmeter leads are designated as the reference junctions. The net voltage, or thermoelectric electromotive force, varies in a known way on the temperature of the measuring and reference junctions. For example, ASTM Specification and Temperature-Electromotive Force (EMF) Tables for Standardized Thermocouples (E 230), ASTM Temperature-Electromotive Force (EMF) Tables for Tungsten-Rhenium Thermocouples (E 988), and ASTM Guide for Temperature Electromotive Force (EMF) Tables for Non-Letter Designated Thermocouple Combinations (E 1751) give reference tables for thermoelectric emf as a function of measuring junction temperature, with the reference junctions fixed at 0 °C. To determine the temperature of the measuring junction, the temperature of the reference junctions must be known. In a calibration laboratory, the reference junctions are generally held at 0 °C by immersion in an ice bath; for a field instrument, the reference junctions are often mounted on an isothermal block whose temperature is monitored by a second thermometer, such as a PRT or thermistor. In the evaluation of temperature measurement uncertainty, the uncertainty of the reference junction temperature must be included.

With thermocouples, extreme care should be taken in the evaluation of drift when the thermocouple is used at temperatures in excess of approximately 150 °C. Recalibration of used thermocouples, except as installed in the apparatus in which the thermocouples are used, is an improper method for the evaluation of thermoelectric drift. In situ comparison tests, where a reference thermometer is placed alongside a used thermocouple in a process environment, provide a desirable alternative method [6]. The drift of base-metal thermocouples (types E, J, K, N, and T in ASTM E 230) will often exceed the maximum scale error of LiG thermometers from ASTM E 1 and E 2251, at temperatures as low as 150 °C, with cumulative drift over 1000 h of use being comparable to the tolerances in ASTM E 230 [7]. Furthermore, a thermocouple that suffers drift is not readily recalibrated. Thermocouple drift is discussed in Refs. [6, 7, 8].

Readouts for thermocouples consist either of a voltmeter used with external reference junction compensation, or of special units containing internal reference junction compensation and programmed with the response curves of E 230, E 988, and E 1751 to give display units of temperature. The response curves of E 230 are identical to those of the international standard [9].

Table 2 lists the uncertainties of a temperature measurement using thermocouples. Thermocouples are an attractive alternative when a thermometer with low cost or small size is desired, and a relatively low accuracy (approximately 1 % of the temperature span across the thermocouple) is acceptable. Noble-metal thermocouples are available with much better uncertainties, but these are most often used for high-temperature applications outside the range of LiG thermometer applications.

Table 2. Uncertainty components for temperature measurement with a thermocouple.

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 [5]
Reference junction uncertainty	Manufacturer or independent evaluation
Readout uncertainty	Manufacturer or independent evaluation
Readout drift	Manufacturer or independent evaluation

Tolerance versus Calibration Uncertainty

A tolerance band is a guarantee by the manufacturer that the response of the instrument will conform to a standard response function to within an error equal to the tolerance. An individually calibrated thermometer, on the other hand, may or may not have a response close to the nominal response function for that thermometer type. Typically, the response of that 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.

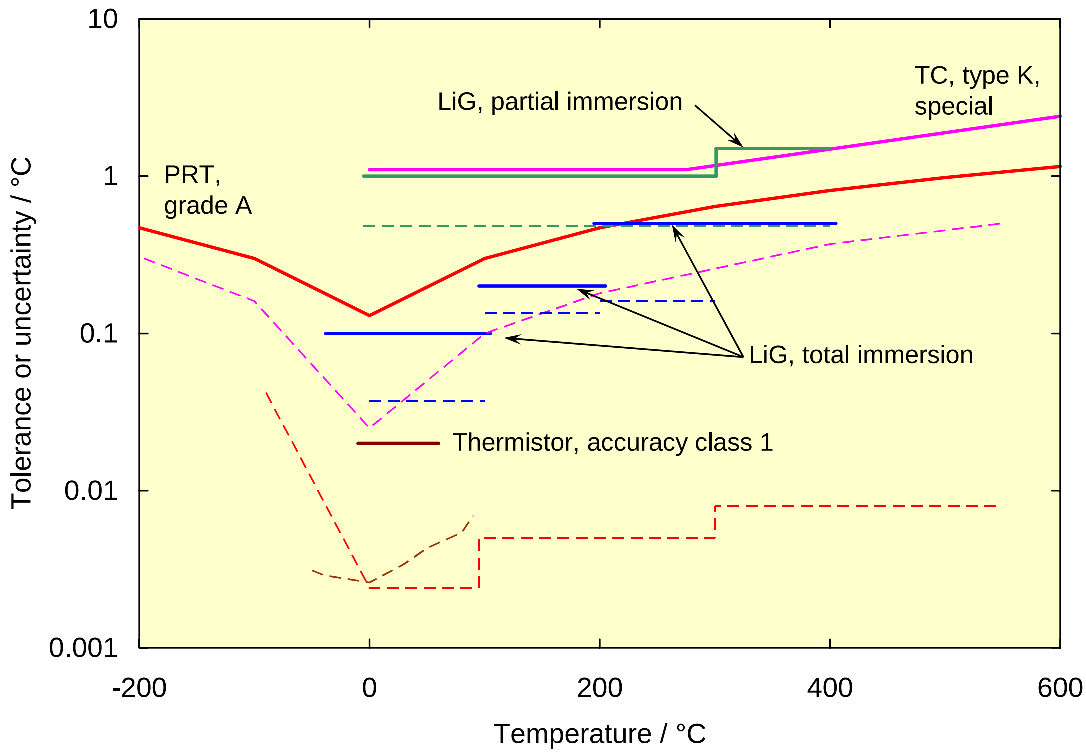

FIG. 1. Colored lines indicate the tolerances of selected LiG thermometers (ASTM E 1), PRTs (ASTM E 1137), thermocouples (ASTM E 230), and thermistors (ASTM E 879). Dashed lines of the same color indicate calibration uncertainties (k=2) for each of these thermometer types, as provided by the National Institute of Standards and Technology.

The solid lines in Fig. 1 show the ASTM tolerances of a small selection of PRTs, thermocouples, thermistors, and LiG thermometers. The dashed lines, matched in color to the solid lines, give the expanded uncertainties (coverage factor k=2) of calibrations of these thermometer types at the National Institute of Standards and Technology. For the best total-immersion LiG thermometers at temperatures above the range of thermistors, it is clear that the ASTM tolerances for PRTs are in general higher than tolerances for the LiG thermometers. This does not imply that PRTs cannot deliver performance equivalent to a LiG; it does imply that a PRT will either need to be manufactured to a tighter tolerance than the standard grade A and grade B tolerances of ASTM E 1137, or that each PRT will need to be individually calibrated. Similar arguments apply for thermocouples. Note that the calibration uncertainties shown do not include such components as sensor drift or readout uncertainty.

Comparison of Uncertainty

Each of the components in Tables 1 and 2, when expressed in units of temperature as a standard uncertainty, should be added in quadrature to obtain the root-sum-of-squares combined uncertainty. The combined uncertainty is multiplied by a coverage factor k to obtain the expanded uncertainty [10]. For normally distributed uncertainties, the expanded uncertainty with a coverage factor of 2 specifies a band containing the true measurement result 95 % of the time. An increased value of k is used to obtain a band with a higher level of confidence. For LiG thermometers specified in ASTM E 1, it is important to note that neither ASTM E 1 nor E 2251 gives an uncertainty of use in all cases. If a LiG thermometer is specially calibrated, the uncertainty may be significantly smaller than the ASTM E 1 or E 2251 tolerance. Optimal uncertainties achievable for the calibration of a LiG thermometer are discussed in Ref. [11]. On the other hand, use for extended periods of time at high temperature may cause drift of the LiG thermometer outside the original manufacturer's tolerance, if not corrected by later recalibration. Whether a LiG thermometer is initially calibrated or not, surveillance of, and possibly correction for, drifts in the ice point are needed to maintain continued validity of the thermometer.

If an alternative thermometer is desired with performance equal or better than a LiG thermometer, the sum of the components, at a coverage factor of 2 or 3 (as chosen for a particular ASTM standard) should not exceed the maximum scale error of the ASTM E 1 or E 2251 thermometer.

In the choice of an alternative thermometer, there are a variety of factors beyond uncertainty that must be addressed. The thermal environment during use, the response time of the sensor, and protection of the sensor from harsh chemicals or moisture may all be important in any one ASTM application.

With these issues in mind, we suggest the following comprehensive guidelines for the specification of alternatives to LiG thermometers as a starting point for discussions within ASTM committees:

1. The alternative sensor should be contained in a stainless-steel sheath of outer diameter no larger than the bulb diameter of the ASTM E 1 thermometer, with an end seal to inhibit ingress of moisture.

2a. When used as a replacement for a partial immersion thermometer, the alternative sensor should be immersed at least as deep as the LiG bulb, when the LiG thermometer is at the specified immersion. If greater immersion is necessary to assure sufficient thermal equilibrium between the test fluid and the alternative sensor, it may be necessary to evaluate the thermal non-uniformity of the test fluid for a particular Test Method. ASTM E 644 describes a method for the measurement of minimum immersion depth of a PRT, and this same method may be used for other types of thermometers.

2b. When used as a replacement for a total immersion LiG thermometer, the center of the alternative sensor is recommended to be placed at a depth equal to the center of the LiG thermometer bulb, when the LiG thermometer is indicating a temperature at the midpoint of the high and low temperatures encountered for a particular Test Method. As in 2a., additional testing may be necessary if there are significant thermal nonuniformities of the test fluid.

3a. PRTs should be fabricated in conformance with ASTM E 1137 using 3- or 4-wire lead connections. Manufacturers offer PRTs that meet tolerance bands of smaller magnitude than the Classification Tolerances of ASTM E 1137, but these are not standardized and may have a reduced temperature range. Because tight tolerances require care in calibration or validation, with a resulting higher cost, a tolerance band should be specified that is consistent with the uncertainty budget of the test method.

3b. Thermistors should be fabricated in conformance with ASTM E 879. Only metal-sheathed thermistor probes are acceptable.

3c. Thermocouples should be fabricated either of soft-insulated wire mounted in stainless-steel sheaths, or of mineral-insulated construction in conformance with ASTM Specification for Mineral-Insulated, Metal-Sheathed Base Metal Thermocouples (E 608). For soft-insulated thermocouples mounted in a sheath, care should be taken that the thermocouple junction is electrically insulated from the sheath and that the thermocouple is in good thermal contact with the sheath. The thermocouple wires, or matching thermocouple extension wires and/or connectors, should extend from the measuring junction to the reference junctions. The length of the metal sheath should be sufficiently long so that any connectors or transition junctions (e.g., see Fig. 6 of ASTM E 608) will be well removed from the test fluid and located in a region of nominally ambient temperature.

Guideline 1 ensures that the probe is protected from exposure to chemicals or water, is self-supporting, and is small enough in diameter to have a reasonable response time.

Guidelines 2a and 2b are chosen so that the immersion of the alternative thermometer in the test medium will be similar to that of the LiG thermometer. Attention to this detail is important primarily in circumstances when the ASTM LiG thermometer is used in a relatively small apparatus or in an apparatus where there may be significant thermal non-uniformities.

Guidelines 3a, 3b, and 3c provide some degree of standardization of the alternative probes.

The approach outlined above is relatively conservative, allowing the replacement of a LiG thermometer with an alternative offering a high degree of confidence that the replacement equals the performance of the LiG thermometer in all important respects. If the overall uncertainty needed for a particular application is significantly larger than the scale tolerance given for the ASTM E 1 thermometer used, or if there is no risk of damage to thermometers without metal or glass sheaths, then a less stringent set of criteria may be appropriate.

Additional Factors

Temperature Nonuniformities

For any given ASTM application, the nature of the thermal environment may be very important. If the temperature of a test material or environment must be known, it is not sufficient to measure the temperature at one location. The thermal uniformity of the material or environment must also be accounted for, in addition to the uncertainty of the temperature measurement.

An ASTM standard may be sufficiently prescriptive that a non-ideal thermal environment will nonetheless be highly reproducible from one laboratory to the next. In this case, there will be a bias between the thermometer temperature and the true temperature of the test material or environment, but there may be a high degree of reproducibility (precision in ASTM terminology) of the results among laboratories.

Bias of Liquid-in-Glass Thermometers

In some ASTM standards that specify use of a particular ASTM E 1 LiG thermometer in a particular apparatus, it is possible that certain errors arise in the use of that particular thermometer, but these errors are common to all users of the standard. There are three common circumstances of these errors for LiG 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 Test Method for Inspection and Verification of Thermometers (E 77) for details).

2. In a number of ASTM test standards, a total-immersion thermometer is used at a fixed, partial immersion, with no correction applied. In such use, the measurement errors may be substantially more than the scale error of the thermometer. Nonetheless, if the test method is sufficiently prescriptive, all users of the standard may incur approximately the same error, and the test method may meet the desired need, as confirmed by measurements of the precision and bias of the standard. 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. For both partial and total immersion thermometers, 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. For alternatives to LiG thermometers, one can check for this error by altering the depth of immersion, provided the test medium is generally isothermal.

In these cases, the temperature reading may be significantly biased from the true temperature even though the precision of the reading is quite acceptable. Care must then be taken that the shift in bias from the use of a different thermometer type is acceptable for the intended use of the standard.

Remarks

The discussion above is not meant to be definitive, exhaustive, or unduly prescriptive. We hope, though, that this material will provide guidance on the technical issues involved in the replacement of a LiG thermometer by an alternative sensor.

Acknowledgments

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