



UNITED STATES DEPARTMENT OF COMMERCE National Institute of Standards and Technology Gaithersburg, Maryland 20899-

User-Friendly Guidance on the Replacement of Mercury Thermometers

This document was developed by the Environmental Protection Agency (EPA) and the National Institute of Standards and Technology (NIST) with assistance from Battelle Memorial Institute under EPA Contract EP-W-04-021.





User-Friendly Guidance on the Replacement of Mercury Thermometers

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June 1, 2010

Despite great strides in the reduction of mercury use in health and home applications, mercury thermometers remain in common use in a variety of laboratory and testing uses. Historically, health care, regulated testing laboratories, and specific industries (e.g., petroleum) have relied on NIST-calibrated or NIST-traceable mercury-in-glass thermometers as stable reference standards of temperature. The use of mercury thermometers has been virtually eliminated in routine hospital use, but a wide variety of regulations and test methods continue to specify mercury thermometers.

Mercury thermometers have several intrinsic advantages:

- stable for long periods
- failure usually is visually apparent
- minimal training or maintenance is required.

However, mercury is a powerful neurotoxin, and the cost of cleaning a mercury spill in industry is several thousands of dollars. Furthermore, many states now restrict the sale of mercury thermometers.

Further adoption of alternatives to mercury thermometers is stymied by the lack of simple, yet technically accurate, guidance to users on the selection and use of alternatives. Furthermore, because many modern thermometers are subject to drift in indicated temperature without apparent signs of damage, users need guidance on appropriate validation methods to ensure the continued reliability of temperature measurements for a large variety of testing or process monitoring applications.

We have developed user-friendly guidance documents and complementary guidance videos that can be used to assist users in converting to non-mercury alternatives with a minimum of cost and effort, while maintaining acceptable measurement uncertainties and traceability. The guidance documents and videos topics include:

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Videos – Phase-Out of Mercury Thermometers Used in Industrial and Laboratory Settings – Available on the EPA Website: http://epa.gov/mercury/thermometer.htm

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Selecting Alternatives to Mercury-Filled Thermometers

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June 1, 2010

Overview

Mercury-filled liquid-in-glass thermometers have a long history of use in a variety of laboratory and industrial applications. Although these thermometers provide excellent performance, regulations on the sale of mercury thermometers limit their continued availability. Mercury spilled from broken thermometers also poses an environmental and safety risk.

Alternatives exist for almost all uses of mercury-filled glass thermometers. The information below gives a brief introduction on the selection and use of these alternatives.

Alternatives to Mercury-Filled Glass Thermometers

Resistance Temperature Detector (RTD) or Platinum Resistance Thermometer (PRT)

Currently, almost all RTDs used for accurate thermometry are made with a platinum sensor, and the term platinum resistance thermometer (PRT) generally is synonymous with RTD. The electrical resistance of the platinum rises as the temperature rises. The readout converts the measured resistance to indicated temperature using either a standard curve or a calibration function for the particular probe being used.

A properly chosen PRT probe and readout can be used to replace almost all mercuryfilled liquid thermometers. For high-vibration applications within the temperature range -100 °C to 150 °C (-148 °F to 302 °F), PRT sensors formed from a platinum film deposited on a ceramic chip work well. For applications requiring broader temperature ranges or better uncertainty, NIST recommends wire-wound PRTs. In both cases, the sensor typically is mounted in a metal sheath.

Thermistor

Thermistors are an excellent choice for temperature measurements in the range -20 °C to 100 °C (-4 °F to 212 °F). Thermistors used as thermometers are composed of a blend of metal oxides whose electrical resistance falls as the temperature increases. The most stable thermistors are sealed with a glass coating. For general-purpose use, the thermistor and wire leads often are mounted in a protective metal sheath. Substantial mechanical shocks, such as dropping the probe on the floor, could break the glass coating on the thermistor, leading to increased drift of the sensor.

Thermocouple

A thermocouple temperature sensor consists of two dissimilar metals, joined at one end to form the measuring junction. The two thermocouple wires must extend entirely from the measurement junction to the readout. If intermediate connections are needed, special connectors must be used. Of all the thermometer types, thermocouples are the best option for applications that involve shock and vibration. The manufacturing tolerances for thermocouples are relatively large, and readouts add an additional uncertainty.

Thermocouples can be insulated with ceramic, fiberglass, or polymer insulations. The insulated thermocouple can be mounted in a metal sheath for additional protection of the sensor.

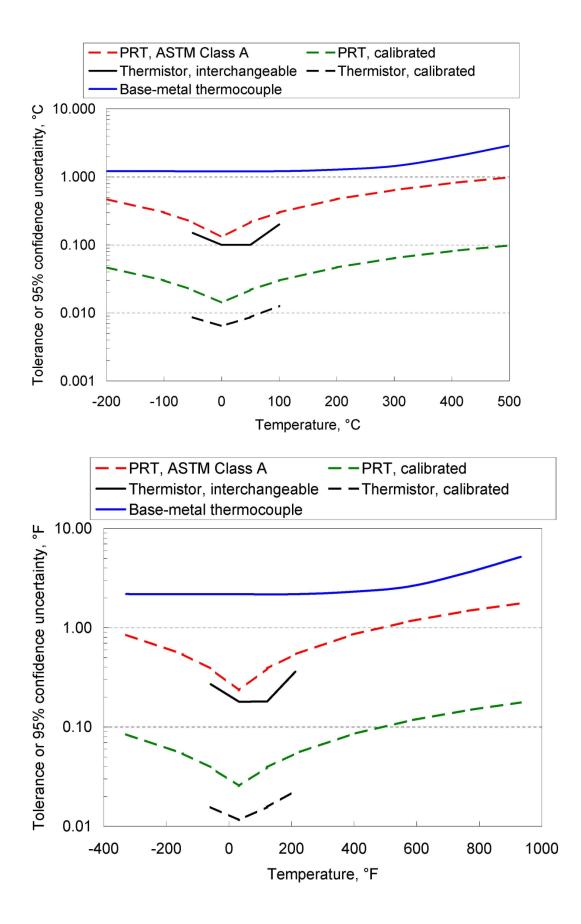
Thermocouples are a good choice when the desired uncertainty is greater than approximately 1 $^{\circ}$ C (2 $^{\circ}$ F), and a mechanically robust or compact sensor is required.

Organic-Liquid-Filled Thermometers

Glass thermometers filled with non-hazardous organic liquids are a good choice when the temperatures of interest are within the range -100 °C to +100 °C (-148 °F to 212 °F), and the desired uncertainty is 0.5 °C (approximately 1 °F) or larger. A wide variety of organic liquids are used for commercially available thermometers. The liquid column of an organic-filled thermometer is subject to separation when the thermometer is shipped, used at extreme temperatures, or stored in a non-vertical position. When an organic-liquid-filled thermometer is subjected to these conditions, the liquid column must be carefully inspected before use.

Chart of Typical Uncertainties

The charts below give a summary of typical achievable uncertainties or manufacturing tolerances, in units of degrees Celsius and degrees Fahrenheit. (These charts can assist with the selection of a thermometer, but do not represent the actual uncertainty of any particular thermometer.) With special care, better uncertainties may be obtained. On the other hand, abuse of the thermometer, long-term use, or use of inferior-quality thermometers can lead to larger uncertainties. The uncertainties on the charts include allowances for sensor drift and readout uncertainties.



Ensuring Good Measurement Results

1. Avoid shock to the sensor and readout. With metal-sheathed thermometers, damage to the sensor will not be apparent from a visual inspection or from a simple operational check.

2. For thermocouples, avoid kinks in the thermocouple wires, especially in regions where the temperature is changing from one point to another. For thermocouples used above 150 °C (302 °F), the best uncertainties are obtained by using a separate thermocouple for each apparatus, and always using the thermocouple at the same immersion depth into the apparatus.

3. Unless you are absolutely certain that two probes are interchangeable, never switch the probe used with a readout without updating calibration coefficients.

4. For readouts that support many types of probes, be absolutely certain that the readout is set to the proper thermometer type (e.g., do not read a Type K thermocouple with a readout set for a Type J thermocouple).

5. Do not exceed the recommended temperature limits for the probe and sensor.

6. Check the performance of the instrument at regular intervals, following the manufacturer's recommendations or past history for the device.

Differences Between Liquid-in-Glass Thermometers and Digital Thermometers

Liquid-in-glass thermometers are self contained and self powered. Glass breakage often indicates mechanical abuse!

In general, digital thermometers cost more than mercury-filled thermometers of comparable accuracy. Readouts for digital thermometers are easy to read, and easy to integrate into an automated data system. These advantages can reduce reading errors and operational costs for digital thermometers relative to liquid-in-glass thermometers. Damage to the sensor for a digital thermometer often is not visually apparent.

Both liquid-in-glass thermometers and digital thermometers require regular validation or recalibration.

Special Conditions of Use

In some standards applications, liquid-in-glass thermometers may be used in a manner that is highly reproducible, but that does not indicate true temperature. Switching to an alternative in these cases can alter a measurement bias in an unpredictable way.

Examples of this effect include:

1. The original liquid-in-glass thermometer was used at an incorrect immersion level. Liquid-in-glass thermometers may be either partial-immersion or total-immersion types. Partial-immersion thermometers have a line around the circumference of the thermometer and/or a printed immersion depth on the back (e.g., 76 MM for 76 millimeters immersion). Thermometers with no indicated depth are the total immersion type. When a partial-immersion thermometer is used, the bottom of the thermometer up to the immersion line should be exposed to the temperature being measured, with the remainder of the thermometer exposed to ambient conditions. When a total immersion thermometer is used, the bulb and the entire portion of the stem containing liquid, except for the last 1 cm, are exposed to the temperature being measured. If the thermometer is not used in this manner, the thermometer immersion is incorrect. In practice, incorrect immersion is not a significant problem if the measured temperature is within 20 °C (36 °F) of ambient temperature.

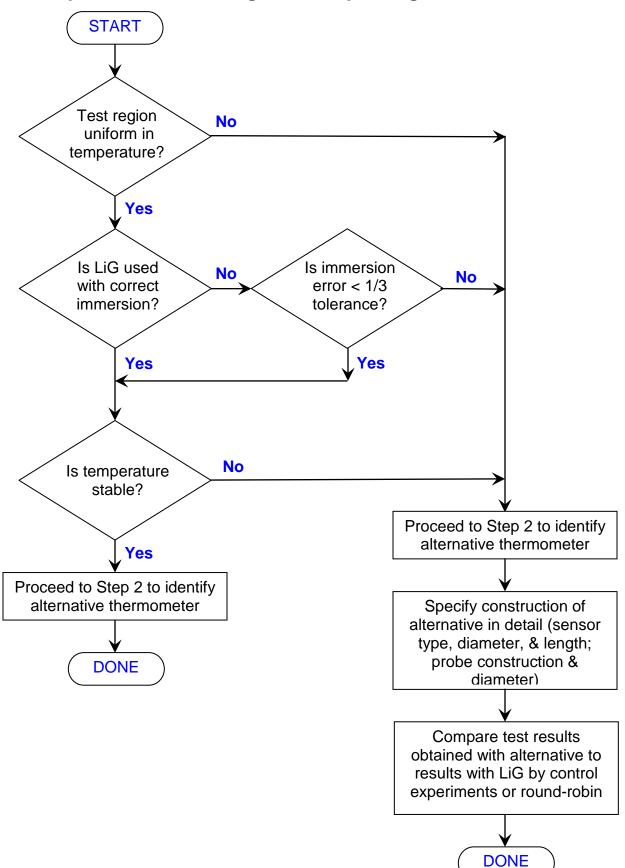
2. The liquid-in-glass thermometer was used for a test where the temperature is not stabilized before a reading.

3. The thermal environment being measured has a temperature that is not uniform.

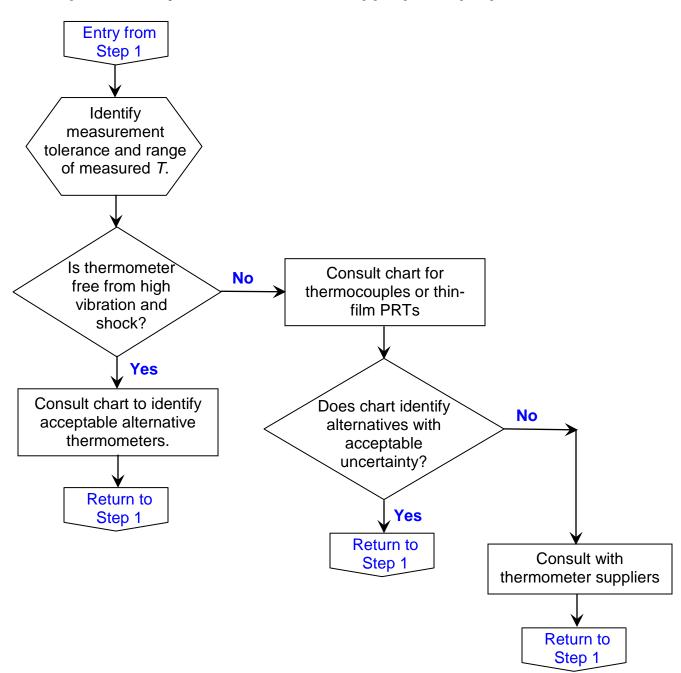
If any of these conditions are true, the reading of a liquid-in-glass thermometer may not correspond to the reading of an alternative thermometer, even if both thermometers are perfectly accurate. We recommend, first, that the alternative thermometer be carefully specified in construction. Second, the readings of a calibrated liquid-in-glass thermometer under these conditions of use should be compared with the readings of a calibrated alternative sensor to identify any measurement bias.

Selection Flow Chart

The selection process described in this document also can be described by a flow chart. Begin with Step 1, and enter Step 2 at the indicated point.



Step 1. Assess the usage of the liquid-in-glass thermometer



Step 2. Identify an alternative with appropriate properties

Frequently Asked Questions

How much does a digital thermometer cost?

Price varies with performance. A digital readout with a thermistor or PRT sensor will cost approximately \$200 for a tolerance of ± 0.2 °C (± 0.4 °F). Thermometers with higher or lower accuracy are available at proportionately higher or lower costs.

Do I need to have my thermometer calibrated? How often?

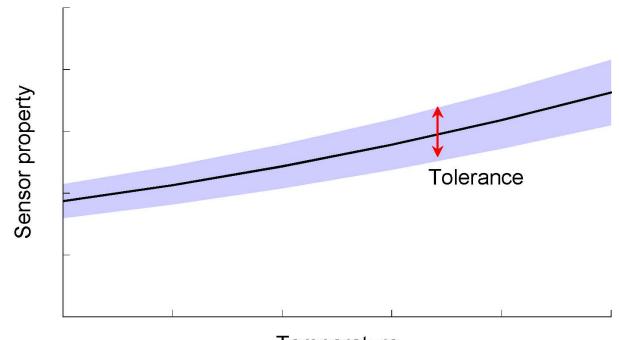
There is no general rule stating whether thermometers require calibration. Thermometers may require calibration because:

- regulations demand calibration or demonstrated traceability to national standards
- thermometer manufacturing tolerances are too large to give the desired accuracy
- the potential risk or cost of trusting an uncalibrated thermometer (which may give the wrong answer) is too high.

See the documents on <u>Maintaining Traceability</u> to NIST for a discussion of how often to calibrate a thermometer.

What is the difference between accuracy, tolerance, and uncertainty?

"Accuracy" is a common term, but it is not well defined. In its most common usage, "accuracy" is the manufacturer's guarantee that the instrument will give the correct answer to within the stated accuracy. In this sense, the word "accuracy" is equivalent to a manufacturing tolerance. A tolerance is the allowed variation in some property of the thermometer sensor, as shown below.



Temperature

Sensors manufactured to meet a tolerance will be interchangeable to within that tolerance, at least when the sensor is new. Remember that thermometers can drift with use. How long a thermometer will meet the manufacturer's accuracy statement depends on the thermometer type and its application!

In the field of metrology, the possible error of a measurement is given as the "measurement uncertainty". The language of uncertainty expresses results in terms of probability. A calibration report might say that at a temperature of 100 °C, a thermometer gave a reading of 99.3 °C with an expanded uncertainty (k = 2) of ±0.4 °C. This language is approximately equivalent to saying:

At a temperature of 100 °C, we obtained a reading of 99.3 °C on your thermometer. There is a 95% likelihood that at a true temperature of 100 °C, your thermometer would read between 98.9 °C and 99.7 °C.

The temperature limits for the thermometer are calculated by adding or subtracting the uncertainty from the measured value: 98.9 °C = 99.3 °C – 0.4 °C, or 99.7 °C = 99.3 °C + 0.4 °C. Different values of *k* (called the coverage factor) correspond to different levels of likelihood, or confidence.

Learning More

General references include:

J. Nicholas and D. R. White, *Traceable Temperatures* (Wiley, 2001).
Handbook of Temperature Measurement (Vols 1-3), ed. Robin E. Bentley (Springer, 1998).

An additional reference for thermocouples is:

3. *ASTM Manual on the Use of Thermocouples in Temperature Measurement*, MNL-12 (ASTM, West Conshohocken, PA, 1993).

A discussion of particular issues for replacing liquid-in-glass thermometers for standards work is found in:

4. Dean C. Ripple and Gregory F. Strouse, "Selection of Alternatives to Liquid-in-Glass Thermometers," *J. ASTM International* **2**, JAI13404 (2005).

How to Ensure That a Thermometer Remains Accurate

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June 1, 2010

Certain types of thermometers are quite fragile. Unfortunately, there are often no visible signs of damage, especially for digital thermometers! The only way to determine for certain that a thermometer's calibration results are still valid is to check its performance.

Here are some methods that can be used to verify the performance of a thermometer. See the guidance on <u>Verification Methods</u> for details on each of these methods, and recommendations on the methods to use for particular types of thermometers. For all of the methods, an allowable tolerance for drift or variability of the thermometer should be established. In regulated applications, the tolerance of the thermometer may be specified; otherwise, the user can select a tolerance based on his or her judgment on the required accuracy. Thermometers that give results outside the allowed tolerance should be recalibrated or taken out of service.

- 1. Periodically have the thermometer recalibrated. If recalibration indicates that the thermometer has drifted by a magnitude that is larger than an allowable tolerance, there are several options available. Improved handling of the thermometer may reduce the drift; a thermometer with better stability can be used; or the interval between calibrations can be shortened.
- 2. Check the readings of the thermometer at the ice point or steam point. The NIST Thermometry Group can provide simple procedures for preparing an ice or steam point.
- 3. Compare the reading of a thermometer to another, recently calibrated thermometer.

Frequently Asked Questions

1. Who has responsibility for ensuring that a measurement is traceable?

Ultimately, the user bears the responsibility of evaluating the traceability chain. NIST does not monitor claims of traceability. There are several items that users can look for as evidence of traceability:

- a. Calibration methods and procedures should be openly documented.
- b. Uncertainties of calibration should be clearly stated.
- c. Traceability records should not be claimed to be private or proprietary knowledge.
- d. Laboratory accreditation is not a guarantee of traceability, but accreditation does provide assurance that qualified assessors have looked at a laboratory's traceability procedures.

2. I have purchased a calibrated thermometer. How often must I have it recalibrated to maintain traceability?

Initial calibration intervals should be based on manufacturer's recommendations or past experience with a type of thermometer. Calibration intervals may be adjusted based on the historical calibration results of a particular thermometer. If check measurements indicate significant drift, then recalibrate. If check measurements indicate large and sudden changes, remove the thermometer from service. See the section on **Learning More** for additional information.

3. Can I do any of the calibrations myself?

You can perform the calibrations yourself if you meet all of the requirements for maintaining traceability and have the necessary laboratory equipment and skills. Users can perform in-house performance checks, such as checks in an ice-point bath. To be sure that you are performing in-house checks correctly, we recommend that users try out their performance checks on newly calibrated instruments that are known to be accurate.

4. My thermometer is traceable to the national standards of another country. Is that equivalent to traceability to NIST?

In some cases, legal or regulatory requirements will explicitly require traceability to NIST standards. If there are no requirements of this type, then the standards of other countries likely are equivalent. Many countries, including the United States, have signed an international Mutual Recognition Arrangement that recognizes the validity of each others' calibration certificates. We also compare thermometers among nations to be sure that our standards are equivalent. Records of the recognized calibration capabilities and of comparison results can be found at http://kcdb.bipm.org.

5. I have a "certified" thermometer that claims to be traceable to NIST. What is the difference between a "certified" and a "calibrated" thermometer?

There is no official definition of "certified." Often, a certified thermometer has been tested against standards traceable to NIST, but the user is given less information on the certificate than is typical for a calibration report. To be sure that the thermometer is truly traceable to NIST, we suggest asking the vendor if the certification followed a documented process, what was the measurement uncertainty, and were the reference standards traceable to NIST.

Learning More

NIST provides a description of traceability and an extensive list of questions and answers on traceability: <u>http://www.nist.gov/traceability</u>. This site is the source for official NIST policy on traceability.

The book *Traceable Temperatures* by J. Nicholas and D. R. White (Wiley, 2001) gives a good discussion of traceability for thermometer calibrations.

To learn more about modern uncertainty analysis, see: <u>http://physics.nist.gov/cuu/Uncertainty/index.html</u>.

To learn more about methods to set calibration intervals, see: <u>"Guidelines for the determination of calibration intervals of measuring instruments,"</u> <u>ILAC-G24, (International Laboratory Accreditation Cooperation, 2007)</u>.

Overview of Verification Methods to Alternatives to Mercury-Filled Thermometers, Including Research on Ice and Steam Points

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June 1, 2010

Part of the process of ensuring that temperature measurements are correct is to verify that the thermometer itself is giving correct readings. Proper design, manufacture, and calibration of the instrument are necessary, but even the best instruments may give readings that are in error. Typical causes of erroneous readings include large mechanical shocks, large thermal shock, drift in the sensor or readout characteristics with time, or incorrect entry of calibration coefficients.

There are many methods for verifying that a thermometer is performing as intended (e.g., within manufacturer specifications). Here, we describe four methods that are especially useful for thermometers in common use. The methods we describe may be used to identify instruments that need repair or recalibration. The methods do not provide guidance for recalibrating the instrument.

For each thermometer or measurement application, you should establish an allowed maximum error, or tolerance. For example, we may require that a refrigerator maintains a temperature in the range 2 °C to 8 °C (35.6 °F to 46.4 °F) for drug storage. The monitoring thermometer should have a tolerance significantly smaller than the total 6 °C (10.8 °F) span from 2 °C to 8 °C (35.6 °F to 46.4 °F), so we can tell with confidence if the refrigerator temperature is close to its limits. Typically, one chooses a thermometer tolerance between 1/10 and 1/4 of the allowed variation in temperature. In this example, if we choose a thermometer tolerance 1/10 of the allowed variation, we obtain 0.6 °C (1.8 °F) as an allowable tolerance for thermometer error.

Recommendations for Different Thermometer Types

Different thermometer types suffer from different types of drift or failure. For example, a glass thermometer has no electronic components that can drift in value, but it does have a liquid column that can separate. Below, we give advice specific to several thermometer types.

Dial or bimetallic thermometers

If used over a narrow band of temperature [within ± 20 °C (± 68 °F) of the ice point or steam point], a single-point verification will suffice. Otherwise, we recommend verification at two points.

Remove from service probes with sticky or erratic needle motion, or if there is evidence of contamination or corrosion beneath the dial glass.

Organic-Liquid-Filled Glass Thermometers

NIST publishes a comprehensive guide on the verification of liquid-in-glass thermometers. These thermometers require visual inspection of the liquid column for breaks in the column if the thermometer has been shipped, stored horizontally, or cooled rapidly. If used in the range 0 °C to 50 °C (32 °F to 122 °F), a check at the ice melting point or at ambient temperature will suffice for verification. If used over a broader range, we recommend combining inspection of historical calibration records with a check at 0 °C (32 °F) or at ambient temperature.

Digital thermometers

Platinum resistance or thermistor sensors inside metal probes may suffer damage (due to mechanical or thermal shock) that is not visibly apparent. If used in a narrow temperature range, a single-point check at a temperature within 20 °C (68 °F) of the usage temperature will suffice. Otherwise, we recommend checking the sensor at the steam point, in addition to checking at either the ice melting point or ambient temperature. If this is not practical, we recommend periodic recalibrations, with inspection of historical calibration records to determine if the thermometers are drifting.

Thermocouples

Thermocouple probes should be inspected for physical damage and kinked wires. Verification at the ice melting point or ambient temperature is an excellent check of the readout, but not a good indicator of probe damage due to mechanical kinks or exposure to high temperatures. If the thermocouple probes are used above 150 °C (302 °F), the probes may drift in ways that are hard to identify by the verification methods we list. Refer to the references section of this document for more guidance.

Four Methods to Verify a Thermometer

Comparison with another calibrated thermometer at ambient temperature

For this measurement, you need to have another calibrated thermometer. You also will need a glass beaker or large cup, tap water at room temperature, a magnetic stir bar, and a magnetic stirring plate, or a hot plate with a stirring option. If you use the hot plate, do not energize the heated plate.

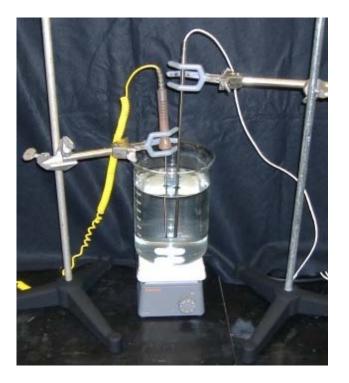
The measurement is straightforward:

- 1. Fill the beaker or cup so that the water is at least 20 cm (approximately 8 in.) deep.
- 2. Let the water sit for 2 h (or ideally, overnight) so that the water temperature is nearly the same as the room temperature.
- 3. Put the stir bar in the bottom of the beaker, place on the stir plate, and adjust to give a slow stir rate. The stir bar should revolve at about one revolution per second.
- 4. Insert the thermometers so that the tip of the probe is 10 cm to 15 cm (approximately 4 in. to 6 in.) below the surface of the water. (If the thermometer probe is very short,

immerse the probe as much as you can without getting water in a dial or in the wiring.)

- 5. Wait 5 min.
- 6. Record the readings of the thermometer you are testing, and then the calibrated thermometer.
- 7. Repeat Step 5 and Step 6, but this time record the calibrated thermometer first, and then the test thermometer.
- 8. If the calibrated thermometer has a correction to apply, make this correction according to the calibration certificate for the results of both Step 5 and Step 6.
- 9. For both Step 5 and Step 6, subtract the corrected reading of the calibrated thermometer from the reading of the test thermometer. The result gives the error of the test thermometer.
- 10. The measured error from Steps 5 and 6 should agree to within the repeatability of the thermometer. If not, try repeating the series of measurements, beginning at Step 4.

The picture below shows what the apparatus looks like.



You can get good results stirring the liquid with a long rod instead of the stir bar, but you must be careful and not hit a sensitive thermometer probe with the long rod!

Inspection of Historical Records

One weakness of the method is that the method gives no direct indication that a *particular* thermometer is performing correctly at the present time. On the other hand, for users who have many thermometers, or a long calibration history of one thermometer, this method gives a good statistical measure of the reliability of a thermometer. This method works best in combination with one or two of the other methods.

To perform this method, the thermometer must be calibrated periodically, and for each calibration, the readings of the thermometer must be recorded at the calibration temperatures with the instrument in the "as found" state. The user then calculates the difference between the "as found" readings with the results of the most recent prior calibration. This difference is the drift of the thermometer.

The drift should be determined for several different calibration temperatures, and for several different individual thermometers or for several calibration cycles of a single thermometer. The magnitude of the observed drift gives the user an indication of the typical drift to be expected for that thermometer (or thermometer type) in routine service.

Measurement at the ice melting point

When ice and water are packed together into an insulated container, the mixture has a temperature of nearly 0 °C (32 °F). We call this mixture of ice and water the ice melting point. The important steps in preparing an ice point are:

- 1. Use water that is distilled, de-ionized, or purified by reverse osmosis for both the water and the ice.
- 2. Be sure that the ice pieces are no bigger than a gumdrop—about 1 cm or 0.5 in.
- 3. Pack the insulated flask so that there is an ice-water mixture from top to bottom.
- 4. When inserting the thermometer, make sure that it is clean, that it is immersed at least 10 cm to 15 cm (approximately 4 in. to 6 in.) (if possible), and that the probe tip is at least 2 cm (approximately 1 inch) from the flask walls and about 5 cm (approximately 2 in.) from the bottom of the flask.

The test thermometer should read 0 °C (32 °F). Any difference from these values is the measured error.

The video below gives all of the details in making an ice melting point that has an uncertainty (at 95% confidence) of 0.01 °C (0.02 °F). If you have access to distilled water and an ice crusher, you can actually achieve an uncertainty of 0.002 °C (0.004 °F). See Reference 1 from NIST for more details on how to make this type of ice melting point.

http://www.epa.gov/mercury/nistvideo/index.html#icepoint

Measurement at the steam point

The steam point is not as commonly used as the ice point, but it provides a good method to verify thermometers at a second temperature. In this method, we create steam by boiling water in a beaker. As the steam rises, it will condense on a thermometer that is colder than the boiling point of the water. This condensation will raise the temperature of the thermometer until it is the same as the water boiling point.

The water boiling point, however, is NOT 100 °C (212 °F)! We need to correct the boiling point temperature for the elevation where you will do the measurement and for the barometric pressure. Luckily, you can readily look up elevation and barometric pressure data on the internet. To perform the calculations, you will need to download one of the steam-point calculators below:

<u>Steam Point – Metric</u> <u>Steam Point - English</u>

To do the measurement, you will need a hot plate, a stainless-steel beaker (or a glass beaker wrapped with aluminum foil on the outer side) at least 20 cm (approximately 8 in.) deep, a clamp to hold the test thermometer in place, and a silicone-rubber sheet to cover the beaker.

Here are some important points:

- 1. The method uses boiling water and generates hot steam! Protect yourself from burns and scalding!
- 2. Because evaporating water leaves behind any salts, the method may be used with simple tap water.
- 3. The beaker should be filled with approximately 4 cm (1.5 in.) of water. If a glass beaker is used, wrapping the outside cylinder with aluminum foil of the beaker helps prevent an error due to radiative cooling of the thermometer.
- 4. A loose-fitting cover on top of the beaker ensures that steam fills the space below the cover. You can cut a disc with scissors from a silicone-rubber baking sheet, with a hole in the middle for the thermometer.
- 5. Heat the water to a rolling, but not violent, boil.
- 6. Use a clamp to hold the thermometer probe above the water, in the steam. The thermometer probe should not contact the boiling water.
- 7. The thermometer probe should be immersed at least 10 cm to 15 cm (approximately 4 in. to 6 in.) into the space where steam collects.
- 8. Wait 5 min., and record the reading of the thermometer.
- 9. While you are waiting, you can use the calculator to find out the temperature of the steam point. Due to fluctuations in the barometric pressure, the steam point temperature may vary during the day.

The test thermometer should read the temperature calculated for the steam point. The test thermometer reading minus the calculated steam point reading equals the thermometer error.

The correction for the elevation of the steam point above sea level is quite large [for example an altimeter pressure of 1013 hPa (29.92 in. Hg) will give a steam point temperature of 99.87 °C (211.77 °F), 99.46 °C (211.03 °F), 98.95 °C (210.11 °F), 97.94 °C (208.29 °F) and 94.89 °C (202.80 °F) for elevations of 30.5 m (100 ft), 152.4 m (500 ft), 304.8 m (1000 ft), 609.6 m (2000 ft), and 1524 m (5000 ft), respectively]. The uncertainty of the elevation limits the uncertainty of the steam point. Using the internet tools discussed in the video below and the steam-point calculator, you can achieve an uncertainty of 0.1 °C (0.2 °F) at a 95% confidence level.

http://www.epa.gov/mercury/nistvideo/index.html#steampoint

What Do I Do If a Thermometer Fails Its Verification?

First, check the instrument to see that you are using it correctly. Is the right probe connected to the readout? Are options for the readout set correctly? Then, repeat the verification measurement to confirm the first measurement.

If the results still show an error greater than the tolerance, the instrument should be removed from service and recalibrated. Do NOT correct the reading by the observed error, unless the thermometer manufacturer recommends that you do so. Large errors may indicate that the instrument needs repair.

If a certain type of thermometer displays more than occasional verification failures, you may need to change either the procedure for handling the thermometer or the type of thermometer you use.

References

1. C. D. Cross, W. W. Miller, D. C. Ripple, G. F. Strouse, "Maintenance, Validation, and Recalibration of Liquid-in-Glass Thermometers," NIST Special <u>Publication 1088.</u>

Report on the Identification of Non-Mercury Thermometers for Validating Autoclave Operating Temperatures

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June 1, 2010

Summary

Maximum-registering mercury thermometers have served for many years to verify proper sterilization of a large range of biological products and waste in autoclaves. Replacement of these thermometers by a non-mercury alternative has been stymied by the absence of obvious alternatives. In this work, we investigated several possible alternatives. Fine-gauge Type K thermocouples and autoclave-rated data loggers performed well in our tests. Although these instruments cost more than mercury thermometers, the benefits of monitoring the full autoclave cycle could increase productivity significantly. We recommend field tests of these types of thermometers. Unfortunately, we found no inexpensive, mercury-free alternative. Maximum-registering thermometers coated with polytetrafluoroethylene (Teflon® PTFE)[†] had performance very similar to uncoated thermometers, and the coated mercury thermometers can significantly reduce the risk of mercury release into the environment if they are not thrown away.

[†]Certain commercial equipment, registered trademarks, instruments, or materials are indentified in this document. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

Background

Maximum-registering mercury thermometers have a long history of use as a simple and inexpensive way to verify sterilization temperatures in the pressurized, steam-filled autoclave environment. In many applications, alternatives to mercury thermometers have been identified readily. In the case of autoclave temperature monitoring, no clearly appropriate alternative thermometer has been identified. Attempts to find an alternative maximum-registering glass thermometer filled with a non-toxic liquid have not succeeded. The use of another possible alternative—digital resistance or thermocouple thermometers—is complicated by the difficulty of passing lead wires into the pressurized environment and by the difficulty of protecting the temperature sensor from the steam. Independent of the technical issues, the increased regulation on the sales of mercury thermometers has led to a sharp drop in the number of manufacturers of mercury thermometers. Even if maximum-registering thermometers are not restricted in use (due to the unavailability of practical alternatives), it is possible that these thermometers will be increasingly hard to obtain.

Site Visits

We inspected three separate autoclave installations and discussed autoclave operation with the users and managers of these sites:

- 1. EPA Environmental Science Center, Fort Meade, Maryland
- 2. Maine Health and Environmental Testing Laboratory, Augusta, Maine
- 3. Biochemical Science Division, National Institute of Standards and Technology (NIST), Gaithersburg, Maryland.

Sites 1 and 2 use maximum-registering mercury thermometers to verify that contents of the autoclave have reached a minimum required temperature. Although a sterilization temperature of 121 °C (249.8 °F) is most common, the EPA laboratory conducts some sterilizations at temperatures as high as 135 °C (275 °F). The users of these sites have not identified any practical alternatives to the mercury thermometers. In the sterilization of certain products, such as media culture, the temperature must be high enough to sterilize the product, but overheating by 10 °C (18 °F) leads to product degradation. Personnel at the Maine Health and Environmental Testing Laboratory informed us that breakage of a mercury thermometer during an autoclave cycle could lead to the whole autoclave being classified as hazardous waste. The clean up, disposal, and purchase of a replacement autoclave could cost several thousands of dollars.

Autoclaves in use vary considerably in their age, size, and method of door seals. The modern autoclaves that were observed have a vertical door that closes automatically on actuation of a switch. An elastomer gasket provides a leak-tight seal. An internal sensor monitors the steam temperature of these autoclaves, but the sensor cannot be placed in the actual autoclave load. Although a few autoclaves now in production come equipped with flexible probes that can monitor the temperature of the autoclave contents, we did not observe this type on the site visits.

Older autoclaves have manually sealing doors in either a horizontal or vertical plane. Furthermore, we were told by Mr. Matthew Sica, Laboratory Certification Officer for the State of Maine, that older autoclaves with limited or no instrumentation were very common in small testing laboratories.

Existing Alternatives

We identified possible alternatives to maximum-registering mercury thermometers by four methods:

- 1. Interviews of autoclave users at EPA and state laboratories
- 2. Interviews of thermometer suppliers and distributors
- 3. Product research on the internet
- 4. Experience with products used at NIST.

Below we discuss each of the possible alternatives.

Liquid-in-glass thermometers

Maximum-registering mercury thermometers function by a unique method. On heating, the mercury in the bulb expands, forcing mercury up the graduated capillary. On cooling, the mercury column separates, leaving the mercury in the column stationary while the remaining liquid in the bulb contracts. The column separation is facilitated by the

geometry of the thermometer and the high surface tension of mercury. Attempts to recreate similar column separations with an organic liquid have not succeeded. Manufacturers have succeeded in a relatively minor alteration to the original design—mercury thermometers are available coated in polytetrafluoroethylene (Teflon® PTFE). The coating greatly lessens the risk of a mercury release into the environment in the event of a thermometer breakage. Unfortunately, Teflon coatings have a different thermal expansion than the underlying glass and may also slowly flow with time. Consequently, thermal cycling of the thermometer can lead to variations in the mechanical force on the thermometer bulb from the coating, possibly leading to higher variability of thermometer readings.

Resistance thermometers

Resistance thermometers are readily capable of measuring autoclave temperatures with high accuracy, provided the thermometers and their lead wires are suitably protected from the pressurized steam environment. We were unable to find any commercial products that satisfied this requirement.

Thermocouples

Thermocouples are rugged instruments that are manufactured to tolerances of approximately ± 1 °C (± 1.8 °F). Although this tolerance exceeds the target tolerance of ± 0.5 °C (± 0.9 °F), thermocouples that will withstand the autoclave environment are readily available. One important practical issue is how to pass the thermocouple wires through the door gasket without a loss in steam pressure.

Data loggers

Data loggers are self-contained instruments that include a temperature sensor, analog electronics to read the sensor, and digital electronics to store and download the readings to a computer. Many data loggers are not suitable for autoclave use. Many are not rated for continuous use at typical autoclave temperatures. Others are rated for water exposure, but not for exposure to pressurized steam. Recently, data loggers rated for autoclave use, at temperatures up to 150 °C (302 °F), have become commercially available.

Summary of possible alternatives

Table 1 briefly lists the advantages, disadvantages, and approximate costs of the possible thermometer types.

Thermometer type	Advantages	Disadvantages	Approximate Cost
Mercury in glass	Inexpensive and easy to use.	Mercury spills may contaminate autoclave and have high clean-up costs; thermometer only indicates maximum temperature.	\$50
PTFE-coated mercury in glass	Inexpensive and easy to use.	Care must be taken to recycle mercury thermometer; thermometer only indicates maximum temperature; PTFE will increase thermometer uncertainties somewhat.	\$60
Thermocouple	Readings can be obtained during autoclave cycle; probe can be easily placed anywhere in autoclave load.	Higher cost; need to pass wires through door.	\$250 readout + \$17 for probe
Data logger with resistance thermometer sensor	Record of complete autoclave cycle is obtained automatically.	High cost; requires computer to access data.	\$500 for logger + \$100 for software and data reader

Table 1. Po	ossible thermomete	ers for autoclave	monitoring.
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Thermometers Tested

Based on our survey of commercial alternatives, we chose the thermometers in Table 2 for further study. We included the uncoated mercury thermometer as a control.

Table 2. Thermometers tested in the present study.

Thermometer type	Notes
Mercury in glass	135 °C (275 °F) maximum graduation
PTFE-coated mercury in glass	135 °C (275 °F) maximum graduation
Type K thermocouple and handheld readout	0.08 mm (0.003 in.) diameter wires (40 gauge) with duplex perfluoroalkoxy (PFA) insulation
Type T thermocouple and handheld readout	0.25 mm (0.01 in.) diameter wires (30 gauge) with duplex PFA insulation
Type T thermocouple and handheld readout	0.51 mm (0.02 in.) diameter wires (24 gauge) with single heavy layer of PFA insulation
Data logger with resistance thermometer sensor	Rated for continuous use at 150 °C (302 °F) and autoclave service

Tests Performed

We conducted all of the calibrations in the NIST Industrial Thermometer Calibration Laboratory, immersing the thermometers in a stirred oil bath and using a calibrated standard platinum resistance thermometer as a reference. The expanded uncertainty (with a coverage factor k = 2) of the calibration measurements did not exceed 0.02 °C (0.04 °F) for all tests, excluding the repeatability of the instruments under test. Autoclave testing was conducted in the autoclaves located in the NIST Biochemical Science Division. The thermometer types were subjected to the following tests:

- 1. Three repeat calibrations at 130 °C (266 °F)
- 2. Three repeat calibrations at 121 °C (249.8 °F)
- 3. Exposure to simulated autoclave environment of 120 °C (248 °C) pressurized steam for 2.5 h
- 4. Calibration at 130 °C (266 °F)
- 5. Exposure to dry heat at 142 °C (287.6 °F) for 87 h
- 6. Calibration at 130 °C (266 °F)
- 7. Comparison of readings in two autoclaves cycled to 121 °C (249.8 °F), for a total of three, 1 h runs
- 8. Calibration at 130 °C (266 °F).

Due to an oversight, the 0.08 mm (0.003 in.) Type K thermocouples were not included in steps 1 and 2. However, we have previously demonstrated that Type K thermocouples have excellent stability at 200 $^{\circ}$ C (392 $^{\circ}$ F).

In addition, we performed several special tests on the thermocouple wires:

- a) We examined the effect of 15 door closings on the readings of a Type K thermocouple.
- b) The insulation resistance of the thermocouple wire was tested after step 3.
- c) After steps 5 and 7, we studied the sensitivity of thermocouple readings to the depth of immersion in the calibration baths.

Results

Figures 1 through 3 show the calibration results at 130 °C (266 °F) for the various thermometer types, before and after exposure to the ovens and autoclaves. Additional calibration data at 121 °C (249.8 °F) were consistent with the results at 130 °C (266 °F) and are not shown.

Maximum-registering mercury thermometers typically are calibrated by exposing the thermometer to a known temperature, removing the thermometer to ambient temperature, and reading the temperature after elapsed times of 5 min. and 1 h. In actual use in an autoclave, the thermometer is cooled over approximately 20 min. in the autoclave, and then removed to ambient, which is a thermal history approximately intermediate between the standard calibration procedures. From Figure 1, note that both the coated and uncoated mercury thermometers drift downward significantly between 5 min. and 1 h after exposure to temperature. The two tested thermometers drop in reading by -0.26 °C (-0.47 °F) at 121 °C (249.8 °F) and -0.30 °C (0.54 °F) at 130 °C (266 °F) between the 5 min. and 1 h points. This degree of drift is somewhat higher than previously observed with similar thermometers calibrated at NIST. On average, the readings of the

thermometers agree with the NIST reference standard by 0.25 °C (0.45 °F), but with a standard deviation of 0.4 °C (0.7 °F).

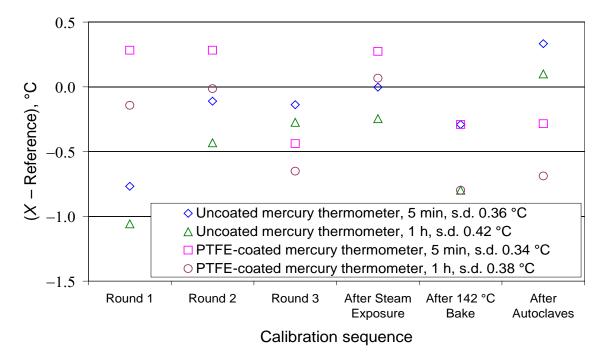


Figure 1. Calibration results for maximum-registering mercury thermometers at 130 °C (266 °F). (Standard deviations of the readings in this and other figures are denoted "s.d.")

Figure 2 shows the calibration results for the thermocouple thermometers. Initially, all of the thermocouples agreed within 0.2 °C (0.4 °F) of the NIST reference. This level of agreement actually is considerably better than expected, because the readout has a tolerance of ± 0.4 °C (± 0.7 °F) and the thermocouple wire itself has a tolerance of ± 1.1 °C (± 2.0 °F). The thermocouples show some sensitivity to steam exposure, especially the Type T thermocouples. The downward drift of the Type T thermocouples, after use in the autoclaves, is of some concern, because this drift occurred over only three autoclave cycles. The Type K thermocouple is very stable, despite its fine diameter.

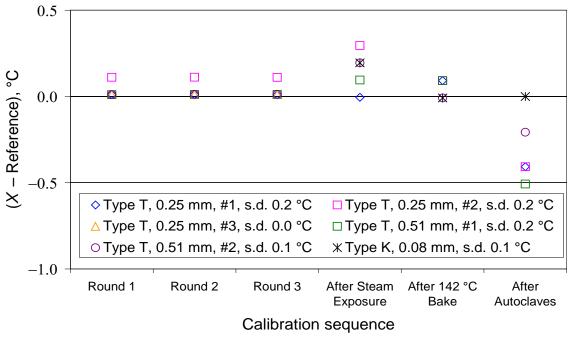


Figure 2. Thermocouple thermometer calibration results at 130 °C (266 °F).

A thermocouple sensor actually generates an electromotive force (EMF) signal along the entire length of its wires, not at the junction. As a consequence, moving segments of thermocouple wire that have been altered chemically (by steam exposure) or physically (by the autoclave door) in or out of the calibration bath can cause changes in the thermocouple reading. Studies of these effects in our calibration bath showed a possible variation of approximately ± 0.2 °C (± 0.4 °F) for thermocouple wires that had been sealed between an autoclave door 15 times successively. The sharper thermal gradients in an actual autoclave could make these effects somewhat larger. We estimate that in the worst case, 15 door closings could cause approximately three times larger drift than we measured, or ± 0.6 °C (± 1.1 °F).

As a final check on thermocouple performance, we measured the electrical resistance of the PFA insulation used on the thermocouples. The duplex-construction wires (the standard form) had electrical resistances that were all higher than 5 M Ω , which is high enough to be negligible. The 0.51 mm (0.02 in.) Type T thermocouple had an electrical resistance of only 5 k Ω , which may be low enough to cause minor shifts in measured voltage.

The calibration results for the data logger are shown in Figure 3. Of all the thermometers tested, the data logger showed the best stability, with a standard deviation of only 0.1 °C (0.2 °F). The data logger readings differed from the NIST reference standard by -0.3 °C (-0.5 °F), well within the claimed 0.5 °C (0.9 °F) tolerance.

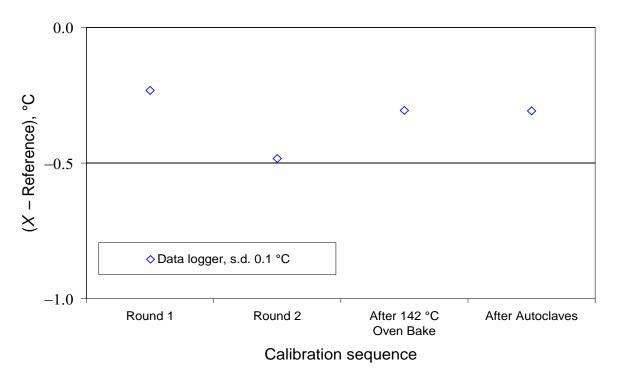


Figure 3. Data logger calibration results at 130 °C.

Figures 4 through 6 show the testing of the candidate thermometers in an autoclave at NIST. The thermometers were bound together to bring the sensors in close proximity. Automated autoclave runs were performed with and without the thermometers covered in 3 cm of water.

As expected, the door seal proved to be a source of problems for the thermocouples. The 0.51 mm (0.02 in.) Type T thermocouple suffered a failure of its insulation at the door seal. Remarkably, the fine-gauge Type K thermocouple incurred no damage, provided the thermocouple was given ample slack while the door closed (see Figure 5). Steam also leaked by the thermocouple wire. The steam loss was acceptable for all the thermocouple types on the autoclave shown in Figures 5 and 6. However, a test run on a smaller manually controlled autoclave had unacceptably high steam losses for the 0.51 mm (0.02 in.) and 0.26 mm (0.01 in.) Type T thermocouples. Steam loss around the 0.08 mm (0.003 in.) Type K thermocouple was minimal.

Figures 7 and 8 show the complete thermal histories as recorded by the various thermometers. Remember that the maximum-registering thermometers are read after removal from the autoclave, and their reading should be compared to the maximum of the other thermometers during the run. The visually obvious insulation failure of the 0.51 mm (0.02 in.) Type T thermocouple led to a large error (Figures 7 and 8). For the other thermometers, the thermocouples are in excellent agreement with the data logger after thermal equilibrium has been achieved. Curiously, the maximum-registering thermometers read significantly higher than any of the thermocouples in steady state or the data logger, by approximately 1.4 °C (2.5 °F). At this time, we do not know if this difference is due to the mercury thermometers registering a spike in the initial

temperature (as seen on one of the thermocouples) or is due to a difference in usage pattern between the calibration procedure and the autoclave procedure.

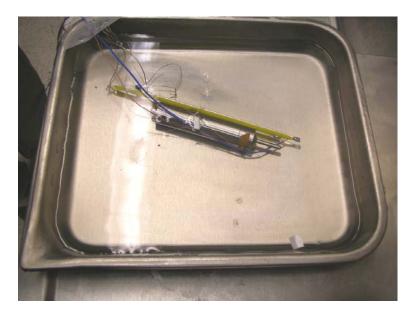


Figure 4. Stainless steel tray holding thermometers for comparison measurements.



Figure 5. Method of closing autoclave door on the thermocouples.



Figure 6. Autoclave door closed, with thermocouples passing through the top door seal.

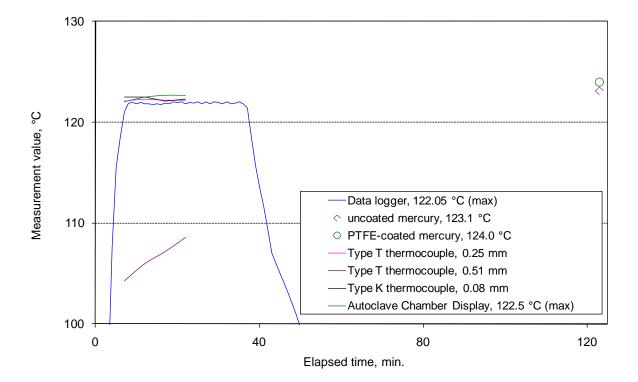


Figure 7. Autoclave comparison in open pan with no water.

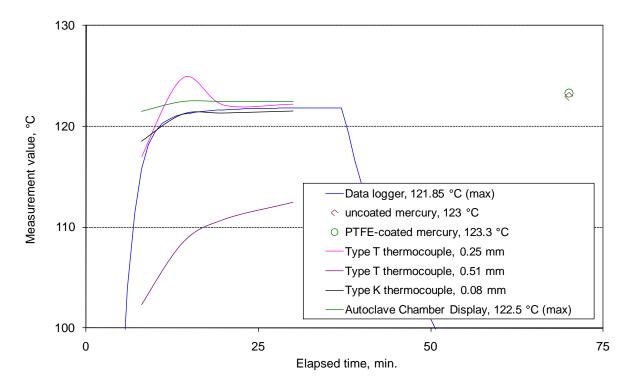


Figure 8. Autoclave comparison in water-filled pan with cover.

Recommendations

The larger gauge, 0.51 mm (0.02 in.) thermocouples often used for autoclave studies suffered problems of steam leakage or insulation breakage for the non-standard insulation type. The 0.25 mm Type T thermocouples served reasonably well, but drifted downward with use and had some minor steam leakage. Remarkably, the very fine 0.08 mm (0.003 in.), PFA-coated Type K thermocouples proved resistant to damage and very easy to use, even for the autoclave with automated doors.

The autoclave-rated data logger satisfied the manufacturer's tolerance through several autoclave cycles and a long bake near its maximum rated temperature.

We recommend field tests that include the fine-gauge Type K thermocouple and the autoclave-rated data logger. The fine-gauge Type K thermocouple proved to be much more durable and easy to use than anticipated. The PTFE-coated mercury thermometer is a less attractive option, because it only limits mercury release rather than preventing release, but it also should be included in the field tests in the event that the thermocouples or data logger prove impractical.

Either a thermocouple and suitable readout or a data logger has a high initial cost relative to a mercury thermometer, but these costs should be compared to the likely gains in productivity. A thermocouple can be monitored in real time, and readouts can measure

the average, maximum, and minimum temperature over a specified time—use of thermocouples can give an immediate, direct indication of adequate interior autoclave temperature without opening the autoclave or heating for excessive times. As a result, runs with improper temperature control are minimized, and run length is only as long as necessary. Data loggers cannot be read during the autoclave cycle, but give a straightforward method of assessing the complete thermal history of the autoclave load with a minimum of operator time or attention to the logger. Proper use of a data logger can optimize autoclave procedures to maximize productivity.

There is an additional, subtle, yet very important advantage in the use of thermocouples or data loggers. For adequate sterilization, one wishes to determine that the autoclave maintained a certain minimum temperature for a specified time. A maximum-registering mercury thermometer reads only the maximum temperature and cannot give any information on the duration of that achieved temperature. In contrast, thermocouples and data loggers give full assurance that the temperature has exceeded a predetermined minimum limit for a specified time.

What is Traceability?

Traceability can be defined as an unbroken record of documentation (e.g., "documentation traceability") or an unbroken chain of measurements and associated uncertainties (e.g., "metrological traceability"). When we use the word "traceability" in this paper, we will always mean "metrological traceability."

The National Institute of Standards and Technology maintains the U.S. national standards for temperature. In other countries, similar national standards laboratories perform the same function.

The readings of a thermometer can be compared to a known temperature standard through the process called "calibration." Once a thermometer is calibrated, it can serve as a standard with a higher uncertainty (lower level of accuracy) to calibrate another thermometer. This process can be continued, providing an unbroken chain of measurements from the final thermometer all the way back to the NIST standards.

When we compare one thermometer to another, the measurement has a probable error. Sources of error could include how well we can read the thermometer, how close the two thermometers are maintained in temperature, and the repeatability of each thermometer. The measurement uncertainty gives a measure of the probable magnitude of all of the combined sources of error.

The final measurement will have traceability to NIST standards if the following conditions are met:

- 1. An unbroken chain of measurements back to NIST standards is maintained.
- 2. Each step of the chain must have known and documented uncertainties.
- 3. There is a system to ensure that the thermometers and associated measurement equipment maintain their measurement uncertainty between calibrations.

Example

The figure below shows a typical traceability path. With proper care, a thermometer can be used through many recalibration cycles beyond what is shown in the figure.

NIST calibrates a platinum resistance thermometer (PRT, shown by the red dot) for a manufacturer against NIST standards (blue dot)

