Thermometry Issues in Destruction Kinetics Measurement

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Overview of thermometer types, terminology, & general issues
Detailed discussion of different thermometer types
Verification & good practice

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Effects of Temperature on Microbes

Small temperature changes:

Arrhenius Equation: reaction rate constant proportional to $e^{-E_a/RT}$

$E_a = \text{activation energy}, \ R = \text{gas constant}, \ T = \text{absolute temperature}$

Modification of protein enzymatic kinetics

Even small changes in temperature, at relatively low temperature, can lead to significant changes in rate of microbial inactivation

Large temperature changes:

Activation of protective pathways (e.g., heat-shock proteins)

Physical alterations to proteins, DNA

Accurate thermometry aids in determination of damage thresholds

**Accurate measurements ensure validity and interchangeability of kinetics data, for both thermal and thermally assisted inactivation**
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. Expanded uncertainties (95% confidence limit, or ‘coverage factor $k = 2’$) typically reported for calibration measurement—not including drift & user readout

Individually calibrated thermometers are not interchangeable, unless the readouts or software are adjusted.
### Typical Measurement Uncertainty Budget

<table>
<thead>
<tr>
<th>Component</th>
<th>Method of evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration uncertainty or tolerance</td>
<td>Manufacturer, calibration report, or tolerance</td>
</tr>
<tr>
<td>Sensor drift</td>
<td>Literature, manufacturer, recalibration, or in situ check</td>
</tr>
<tr>
<td>Readout uncertainty</td>
<td>Manufacturer or independent evaluation</td>
</tr>
<tr>
<td>Temperature stability</td>
<td>Logging of temperature</td>
</tr>
<tr>
<td>Temperature non-uniformity</td>
<td>Move probe or use multiple probes</td>
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*Note that only the first item is included in the initial calibration or manufacturing tolerance*
Thermometer Types

Standard Platinum Resistance Thermometers (SPRTs) $6000
(very accurate, but susceptible to shock)
–259 °C to 962 °C

Industrial Platinum Resistance Thermometers (IPRTs) $200 to $2000
–196 °C to 850 °C

Thermistors $200 to $2000
–50 °C to 100 °C

Thermocouples $100 to $1000
–196 °C to 2100 °C

Liquid-in-Glass Thermometers $20 to $400
–150 °C to 400 °C

Digital Thermometers (PRT, thermistor, or thermocouple in disguise)
–196 °C to 850 °C
Approximate Measurement Uncertainties of Complete Systems

- PRT, ASTM Class A
- PRT, calibrated
- Thermistor, interchangeable
- Thermistor, calibrated
- Base metal thermocouple
- Organic liquid-filled

![Graph showing approximate measurement uncertainties of complete systems across different temperature ranges.](image-url)
Types of Liquid-in-Glass (LiG) Thermometers

Types of ASTM LiG thermometers
- Over 120 types
- Total Immersion: immerse thermometer nearly up to top of capillary
- Partial Immersion: immerse a designated, fixed depth (e.g., 76 mm)

Liquids used
- Mercury (Hg) – ASTM (sales regulated)
- Organic
- Proprietary (non-toxic)
Non-Mercury Liquid-in-Glass Thermometers

- Organic liquids generally have inferior performance to mercury, but are a reasonable alternative if uncertainty requirements are modest.

- Beware of drainage of organic liquid down capillary wall on cooling.

- “Next-generation” organic liquids under development (Existing ASTM standard E2251); good accuracy, but check for separation of liquid column.

- Greater sensitivity to stem temperature: a fundamental limitation for partial immersion thermometers—total immersion preferred.

- Best results for use at steady operating temperatures, within range –100 °C to +100 °C; attainable expanded uncertainties of approximately 0.5 °C to 1 °C for properly used total immersion.
Thermocouples

Standardized combinations of Material A vs. Material B (e.g., Type K).

When combined with typical readout uncertainty, total uncertainty is fairly large, unless care is taken with calibration.

Good for low-accuracy measurements over a broad temperature range

Type K is a good choice for sterilization applications; typical drift of 0.3 °C over one year at 200 °C, for fixed installation
Soft-Insulated Thermocouples

- Fluorocarbon insulations suitable to 200 °C (392 °F)
- Note that method for forming junction does not matter!

Mineral-Insulated, Metal-Sheathed (MIMS) Thermocouples

- MIMS thermocouples are available in small diameters (0.25 mm)
- Sheath protects thermoelements from contamination & simplifies sterilization
Effects of Pressure on Thermocouples

Bare-wire thermocouples readily withstand high-pressure environments

Pressure distorts atomic lattice of thermoelements, resulting in small shifts in thermoelectric response.

Thermocouple measurements may be useful in understanding/validating models of adiabatic heating.

Errors are small for typical pressures ~ 400 MPa

Error for type K = \((-2.3 \times 10^{-6})\Delta t(p/\text{MPa})\)

Error for type S = \((-1.9 \times 10^{-5})\Delta t(p/\text{MPa})\)

where \(\Delta t\) = temperature span of thermocouple, \(p\) = pressure in MPa

e.g., Error for type K spanning 100 °C at 400 MPa is only –0.09 °C

R. Hanneman, Symposium on the Accurate Characterization of the High-Pressure Environment, Oct. 14-18, 1968, Gaithersburg, MD
Platinum Resistance Thermometers (PRTs)

Resistance element
  • Wire wound (most accurate, or for wide temperature range)
  • Thick or thin film (rugged)

Resistance increases as a function of temperature

Nominal temperature range of use:
  • –200 °C to 850 °C

Nominal resistance at 0 °C
  • 100 Ω for wire wound
  • often higher for film

PRTs are most common “Resistance Temperature Detector” (RTD)

Steel sheath containing sensor

Sensor or element (wire-wound shown)
Calibrate individual units for lower uncertainty
Which Industrial PRT (IPRT) Should I Use?

Probes vs. Bare Element: probes recommended unless element is permanently mounted. Note that moisture seal at top of probe is NOT resistant to autoclaves/steam sterilization.

Film IPRTs: good time response, small size, shock resistant; not as good as wire-wound over large (>200 °C) temperature spans. Drift after 365 cycles to 160 °C ≈ 0.2 °C.

Wire-wound IPRTs with constrained coils: low accuracy, but shock resistant. Drift after 365 cycles to 160 °C ≈ 0.1 °C.

Wire-wound IPRTs with slightly constrained coils: best accuracy (approaching ±0.01 °C over 400 °C span), sensitive to shock. Drift better than constrained coils, but highly variable among units.

Resistor configuration
- 2-wire for non-demanding applications (±5 °C)
- 3-wire for ±1 °C measurements, or ±5 °C over long cables
- 4-wire for all high-accuracy measurements
Thermistors (Thermal Resistor)

Semiconductors of ceramic material made by sintering mixtures of metallic oxides such as manganese, nickel, cobalt, copper, iron and uranium.

**Temperature Range:** –50 °C to 100 °C

**Standard Sensor Forms:**
- **bead** 300 Ω to 100 MΩ
- **probe** bead in glass rod

**NTC:** Negative Temperature Coefficient - The vast majority of commercial thermistors used as thermometers are in the NTC category.

**Commonly packaged in stainless-steel sheaths**

**Good choice for applications near room temperature**

**Use only glass-coated variety:** 1-year stability <0.01 °C up to 90 °C; much higher drift at higher temperatures
What is a Digital Thermometer?

An electronic measurement box that converts either resistance or emf of a thermometer to temperature.

ASTM specifications for thermocouples, PRTs, thermistors pertain to sensor or probe only, not complete thermometer.
Digital Thermometers

• Device displays temperature directly by using the calibration coefficients of the thermometer

• Uncertainty: 0.001 °C to 1 °C; Resolution: 0.0001 °C to 1 °C

• Careful use requires careful reading—look at manufacturer’s specifications & know the probe type and limitations

• “Digital Thermometer” only means that you can watch the numbers on a display—no guarantee of better uncertainty

• Calibration can be as a system or as readout + separate probe
  
  System calibration is cheaper and simpler
  
  Probe and readout calibration allows easier repair if one element fails, allows identification of source of drift
Traceability of Temperature Measurements

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

• An unbroken chain of measurements back to NIST standards must be maintained.
• Each step of the chain must have known and documented uncertainties.
• There must be a system to ensure that the thermometers and other equipment used remain accurate between calibrations.

Common misunderstandings:

• Traceability only applies to measurements, not devices
• Traceability does not imply a particular level of uncertainty
• There is no limit to how many transfers may take place between the highest-level standards and the final thermometer, as long as the uncertainty is properly calculated.
Ensuring Good Measurements

1. **Avoid shock to the sensor and readout.** With metal-sheathed thermometers, damage to the sensor will not be visually apparent.

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), best uncertainties are obtained by using a separate thermocouple for each apparatus, at a fixed depth into the apparatus.

3. **For resistance thermometers,** calibrate and use with same lead configuration & excitation current

4. **Do not switch probes** unless probes are interchangeable or coefficients are updated.

5. **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 type J).

6. **Do not exceed the recommended temperature limits.**

7. **Check the performance of the instrument regularly,** following manufacturer’s recommendations or past device history.
Rules of Thumb for Installation Effects

- **Probe location:** understand the temperature differences between the probe location and the microbes of interest as a function of time (e.g., thermal modeling, study of wall vs. product temperature)

- **Avoid large air gaps around probe:** still air is a very poor conductor (500x worse than stainless steel)—can lead to large errors for measurement of temperature transients. Keep gaps small, or use grease.

- **Design measurement geometry** so at least 15 cm (6”) of probe is at temperature of interest. (Use fine diameter probes if this is not possible.)

- **For fluids, physical state & conditions of flow are critical:**
  - **Still gas** (e.g., gas convection suppressed in insulation)
  - **Flowing gas** (e.g., convection oven)
  - **Condensing vapor** (e.g., steam in an autoclave)
Thermometer Verification Methods

1. Periodically have the thermometer recalibrated.
   If recalibration indicates that thermometer drift exceeds an allowable tolerance:
   • Improve handling of the thermometer
   • Choose thermometer with better stability, or
   • Shorten interval between calibrations.

2. Check the readings of the thermometer at the ice (0 °C, 32 °F) and/or steam point (near 100 °C, 212 °F).
   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.
Electromagnetic Interference

Not a major issue for laboratory-scale experiments with well-designed electronics

Design:
- Noise rejection can be hard to glean from manufacturer’s readout specifications; specifications for digital multimeters are better.
- Avoid long cable runs
- Use twisted pair for shielding against 60 Hz noise
- If radio-frequency interference causes problems, add an outer grounded shield
- Use probes with sensor isolated (“ungrounded”) from probe wall

Diagnosis:
- While continuously monitoring temperature, shut off sources of electrical noise. If EMI is a problem, temperature will show a step change (actual temperature change will show a change in slope).
Learning More

Good general guides:

*Traceable Temperatures* by J. Nicholas and D. R. White (Wiley, 2001)


Additional reference for thermocouples:


Modern uncertainty analysis:


Methods to set calibration intervals, see:

“Guidelines for the determination of calibration intervals of measuring instruments,” ILAC-G24, (International Laboratory Accreditation Cooperation, 2007).