A Digitally Linearized Thermistor Thermometer Referenced to IPTS-68

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We describe a digitally linearized thermistor thermometer that is accurate to ±0.01 °C from 0 to 60 °C at a wattage of 50 μW and a sampling time of 1 s. It is traceable to the International Practical Temperature Scale of 1968 (IPTS-68). Analog and digital outputs are provided, the latter as ASCII RS-232C. The thermometer is a 10-cm long, immersed, 1.5 mm diameter probe. Only 0.5 cm of the probe need be immersed, with proper heat sinking of at least 1 cm of the remaining 9.5 cm, for accurate readings. Error from self-heating of the thermometer is less than 5 X 10⁻³ °C at all power settings from 50 to 1 μW.

Additional Keyphrases: calibration • quality control • reference materials

Development of a thermometer that could be referenced to the International Practical Temperature Scale IPTS-68 (1) for use in the biochemical and clinical laboratory has been of considerable interest since the last Temperature Symposium Round Table on Clinical Thermometry (2). Although several simple digital systems for measuring temperature have become commercially available, none has yet appeared that could be used as a secondary standard referenced to IPTS-68 and at the same time provide a linear output over the range 0 to 60 °C that would be usable for both calibration and control. The problem of temperature control and specification has been addressed by the American Association for Clinical Chemistry and by the International Federation of Clinical Chemistry Committee on Standards (3). An appreciation of the very large effect of temperature on the measurement of enzymes and substrates by kinetic methods has prompted these organizations to set as a goal the specification of the temperature at which measurement in the clinical laboratories is made to ±0.05 °C absolute if interlaboratory comparisons of normal values are to be made to ±1% (4). This, of course, is even more imperative for biochemical kineticists and thermal chemists. In partial response to this need, the Temperature Measurement and Standards Division, National Bureau of Standards (NBS), has developed a short-stem Hg-in-glass standard thermometer, which can be read to 0.05 °C (NBS special publication 260-48, SRM 933 and SRM 934). Although this is very useful, it does not help the investigator know the temperature in the reaction cell and, in addition, a continuous readout is clearly not available.

In anticipation of this need, we have been working to improve the inherent stability of the oxides with which the thermistor is made, to decrease its contact noise to the level of the Johnson noise, and to devise instrumentation that would allow us to take advantage of its sensitivity and small size while at the same time providing a linear output over the usual laboratory range for both reference and control.

This paper describes the NBS-IPTS-68 traceable S-10 reference thermistor and a completely digital bridge, linearized and accurate to ±0.01 °C from 0 to 60 °C at wattages of 50 to 1 μW. The wattage is kept constant over the entire temperature range.

Materials and Methods

Calibration

The S-10 thermistor standard consists of an ultra-stable glass probe thermistor encapsulated in a thin-wall stainless-steel tube. The basic semiconductor element is a bead of manganese, nickel, and cobalt oxides mounted on 0.1-mm platinum wires. The thermistor is processed for long-term stability by aging at various temperatures for 16 weeks. During this process, stability data are verified. The completed sensor is finally calibrated by use of a system traceable to the IPTS-68. Temperatures are established at 0, 15, 25, 30, 32, 37, 50, and 60 °C by use of an aluminum integrating block and a precision controlled-temperature oil- or water-bath. The block temperatures are controlled to within 0.0002 °C while the temperature is monitored with a 25 Ω standard platinum resistance thermometer (5) that has been calibrated by NBS. The resistance of the S-10 temperature standard is measured with a Model 4737 Wheatstone bridge (Leeds and Northrup, North Wales, PA 19454). A bridge accuracy of 0.005% is verified before and after calibration by using a Model 9975 comparator bridge (Guildline Instruments, Ltd., Smith Falls, Ont., Canada) and NBS-type four-terminal standard resistors. The comparator bridge has an accuracy of 0.0002%, the resistor standards an accuracy of 0.001%.

Heat Dissipation

The dissipation constant of the S-10 Temperature Standard was found to be 6.6 mW/°C. During calibrations of the platinum resistance thermometer (5), the power across the thermistor was maintained at <0.26 μW.

When the S-10 is used in the digital bridge, the power is kept constant at 1, 5, 10, 25, and 50 μW. The thermistor is allowed 3 h to come to equilibrium at each bath temperature.

Heat dissipation in water in a 1-cm cuvette, estimated from the Finite Element Simulation Technique (F.E.S.T.) (6) Program ACPH (available upon request from the authors), has been shown to depend on the power, the size of the thermistor, the size of the measurement cell, and the velocity of stirring. We used the Mil Specification method (Mil-T-23648A-Sec. 3.13) for a 1-cm cuvette 3 cm deep, to compare theory and experiment under actual working conditions. A detailed discussion of the characteristics of internally heated thermistors has appeared recently (7).

One problem that exists with any resistive temperature

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sensor is the noise and error caused by self heating. The former is a square-root effect with temperature, but the latter is directly proportional to the power across the thermistor. If we assume that we leave the thermistor at the measuring point long enough for a steady state to be established (8),

\[ \nabla^2 T = 0 \]  

(1)

where \( T \) is the temperature, and \( \nabla^2 T = \frac{\partial^2 T}{\partial r^2} + \frac{\partial^2 T}{\partial \phi^2} \). We assume spherical symmetry and a 1.5-mm diameter of the thermistor bead with its glass coating. Then, because the flow of heat must be constant, the temperature gradient is \( \partial T/\partial r \), and the quantity of heat flowing per second is

\[ 4\pi r^2(\partial T/\partial r)K = \text{constant} = EI \]  

(2)

In the case of constant electrical power being supplied, the difference in temperature between the inner and outer spheres will be given by

\[ T_1 - T_2 = EI(r_2 - r_1)/4\pi r_1 r_2 K \]  

(3)

where \( K \), the thermal conductivity, is in W m\(^{-1}\) K\(^{-1}\), \( r_1 \) is the radius of the bead, and \( r_2 \) is the radius of the water shell. For a power supply of 10 \( \mu\text{W} \), the temperature of the thermistor increases by about 10\(^{-3}\) °C. This is particularly important in the case of a measurement made in a small cuvette, i.e., 1 x 1 x 3 cm or smaller, as is generally used in the clinical laboratory.

The measurement system, digital bridge, and computer (Figure 1) consists of a modified Wheatstone bridge, an Intel (Intel Corp., Santa Clara, CA 95051) 8080 microprocessor, and 32k of random access memory (RAM). The input/output to the bridge is through the parallel ports. The bridge is driven by a 16-bit digital-to-analog converter (Model DAC-HR-16B; Datel/Intor, Inc., Mansfield, MA 02048).

We calibrated the S-10 Temperature Standard as described above and then fitted the resistance temperature curve to the equation

\[ R_T = R_{25} \cdot C \exp(A_0 + A_1/T + A_2/T^2 + A_3/T^3) \]  

(4)

The constants \( A_0, A_1, \) and \( A_3 \) were derived from the solution of simultaneous equations with use of the data obtained at 0, 30, and 60 °C. The constants were then used to compute the resistance value, \( R \), at 15, 25, 32, 37, and 50 °C. If all computations agreed with calibration results to within ±0.0015 °C, the data were considered to be valid. The constants for our S-10 (serial number 112), the particular thermistor used in our experiments, were as follows:

\[ R_{25} = 3997.38 \text{ ohms} \]  
\[ A_0 = -12.57464144 \]

A\(_1\) = 3999.985581  
A\(_3\) = 14299193.90

More recently, we have used the resistance temperature calibration data in a polynomial regression-analysis program (9) to obtain the constants for the equation

\[ R_T = R_{25} \cdot C \exp(B_0 + B_1/T + B_2/T^2 + B_3/T^3) \]  

(5)

When this is done, all of the constants are significant, i.e., non-zero, and the curve fit is usually much better than 0.001 °C.

This equation, with an input request for the constants, is programmed onto the RAM board, which generates a look-up table. Thus, when a voltage appears, it is compared with values from the look-up table at every 0.1 °C change and linearly interpolated to the nearest 0.005 °C. This lower limit is set by the 14-bit accuracy of the analog-to-digital converter (Figure 1) (Datel ADC-149B), i.e., 1 part in 16,384. For 0 to 60 °C, ±0.005 °C is 1 part in 10\(^4\), while 14 bits is 1 part in 1.6 x 10\(^4\). Figure 1 diagrams the bridge and control circuits, and shows that several output options are available. Built into the instrument are a small thermal printer and a control program resident in "read only memory" that permits the stored data to be put out to the RS232 ports or through an acoustic coupler to a larger computer, such as the DEC-10 (Digital Computer Co, Maynard, MA). The systems were designed to have four modes of operation, which primarily are concerned with the rate at which data can be taken.

**Results**

The system has been tested in two ways. First, we checked the overall stability and noise of the system electronics by connecting a Vihsay Precision Decade resistor, Model 1304 (Vihsay Resistive Systems Group, Manerin, PA 19355), in place of the thermistor standard. The decade was then set to simulate the resistance of the S-10 Temperature Standard at the desired temperature points. Tests were conducted at various sampling-time intervals and at wattages of 1 and 50 \( \mu\text{W} \). Table 1 summarizes these test results. These tests were

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**Table 1. Electronic System Test with Use of a Vihsay Decade Resistor**

<table>
<thead>
<tr>
<th>Power, ( \mu\text{W} )</th>
<th>Sample time, 1 s</th>
<th>Sample time, 0.01 s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp.</td>
<td>SD</td>
</tr>
<tr>
<td>At 0.000 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.007601</td>
<td>0.01155</td>
</tr>
<tr>
<td>5</td>
<td>0.013425</td>
<td>0.01055</td>
</tr>
<tr>
<td>10</td>
<td>0.017666</td>
<td>0.004491</td>
</tr>
<tr>
<td>50</td>
<td>0.006192</td>
<td>0.004491</td>
</tr>
<tr>
<td>At 25.000 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>25.013732</td>
<td>0.015358</td>
</tr>
<tr>
<td>5</td>
<td>24.979868</td>
<td>0.010071</td>
</tr>
<tr>
<td>10</td>
<td>24.977769</td>
<td>0.005820</td>
</tr>
<tr>
<td>50</td>
<td>24.985738</td>
<td>0.005477</td>
</tr>
<tr>
<td>At 36.600 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>36.603353</td>
<td>0.026295</td>
</tr>
<tr>
<td>5</td>
<td>36.583717</td>
<td>0.010690</td>
</tr>
<tr>
<td>10</td>
<td>36.596547</td>
<td>0.007640</td>
</tr>
<tr>
<td>50</td>
<td>36.601377</td>
<td>0.004990</td>
</tr>
<tr>
<td>At 50.000 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>50.006538</td>
<td>0.022587</td>
</tr>
<tr>
<td>5</td>
<td>50.007715</td>
<td>0.006357</td>
</tr>
<tr>
<td>10</td>
<td>50.005229</td>
<td>0.004739</td>
</tr>
<tr>
<td>50</td>
<td>50.031051</td>
<td>0.000000</td>
</tr>
</tbody>
</table>
conducted in accordance with the prescribed procedure for the calibration of the platinum resistance thermometer (I, 5).

The S-10 Temperature Standard was then connected to the system and immersed into the temperature-controlled oil bath at the desired temperatures. After allowing the thermistor standard to come to equilibrium in the bath, we repeated the tests at the same sampling intervals and wattage settings. These results are summarized in Table 2.

**Discussion**

The above results indicate that, with 50 μW supplied to the thermistor and within the limits of ±0.1 °C at a sampling rate of once per second, this system offers an excellent laboratory temperature standard, traceable to NBS, producing a linear thermistor output that is suitable for both measurement and control. Its speed (one data point per millisecond) and high accuracy bring thermal titration measurements to the same level of precision as spectrophotometry. With modifications it can be used in a differential arrangement such that by limiting the range to ±0.1 °C a sensitivity of ±10⁻⁵ °C can be achieved. A simplified version for use in a spectrophotometer cuvette or water bath currently is being constructed.

The recommendations of Mangum and Thornton (10, 11) that the gallium melting point, 29.7714 °C, be used as the temperature to which all clinical tests be referenced has much to recommend it. This would provide, along with the water triple point, two IPTS-68 points readily available to the Standards Laboratory of a hospital for a constant check on the S-10 and clinical thermometers. Although 37 °C may still be needed for certain tests, the use of thermistors, such as the one described here, would greatly enhance the ability for clinical laboratories to know, referenced to IPTS-68, at what temperature they are in fact carrying out their measurements.

**References**


