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A Low-Noise Thermistor Bridge for Use in Calorimetry

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A precision thermistor bridge and thermistor is described for use in a thermal titration calorimeter or a high-speed stopped- or continuous-flow calorimeter of the Roughton type. These are compared and evaluated with regard to several other types of detectors, including the platinum resistance thermometer, thermocouple, transistor thermometer, and capacitance thermometers. At this time the best detection for our purpose seems to be a specially constructed 20–100 kΩ thermistor used in conjunction with a new ac lock-in amplifier bridge. The sensitivity of the system is equivalent to a peak-to-peak noise of 25×10^{-6} °C, with a 100-ms time constant and 1 μW power dissipation in the thermistor. Long-term drift of the bridge, without an oven, was 1×10^{-6} °C/min.

Precision temperature-measurement has traditionally been done with thermocouples or platinum thermometers (*1*). Recently there has been increased interest in thermistors (*2*), capacitive sensors (*3*), and transistor sensors (*4*). Thermistors have been limited by long-term instability, and noise well in excess of the theoretical thermal agitation noise. These problems are now being solved by improvements, and thermistors appear very attractive for many purposes (*2*).

This paper discusses the merits of thermistors relative to other techniques, reviews the calculation of signal-to-noise (S/N) ratio, and describes optimum application to the measurement of very small but rapid temperature changes in chemical kinetic experiments (*5*), where self-heating must be held to a very low level. The measurement system is also well suited to evaluation of thermistor characteristics.

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Measurement with a thermistor is basically the same as with a platinum thermometer, and the same basic configuration is appropriate, namely, an ac bridge in which the sensor is one arm, followed by a lock-in amplifier. The use of ac eliminates the effect of changing thermal emf's and amplifier drift, and allows amplification at a frequency free from low-frequency noise.

The Bridge

The main advantages of a thermistor are its high temperature coefficient and high resistance. The latter permits direct coupling, with a near-optimum noise figure, and also decreases problems with parasitic series resistance. A block diagram of the bridge is shown in Figure 1. The basic bridge is a standard Wheatstone type. Assuming that $R_2 = R_3$, the bridge is balanced by adjusting R_1 to be equal to R_t. The output e_o resulting from a small change in R_t will be

$$
\begin{aligned}
e_o &= \left(\frac{R_t + \Delta R_t}{2R_t + \Delta R_t}\right) E - 1/2\, E \\
&= \frac{E}{4} \times \frac{\Delta R_t}{R_t} \\
&= \frac{E}{4} \times (T.\,C.) \times \Delta T
\end{aligned}
$$

where $(T.\ C.)$ is the temperature coefficient and ΔT the temperature change.

The thermal noise of the left side of the bridge can be made negligible compared to that of the right side by simply making R_2 10-fold smaller than the thermistor resistance. The noise signal will be essentially that of the right side, with an equivalent resistance $R_t/2$. Therefore $e_n = \sqrt{2kTBR_t}$ in volts r.m.s., where k is Boltzmann's constant, T is the absolute temperature, and B is the bandwidth. The signal-to-noise ratio is

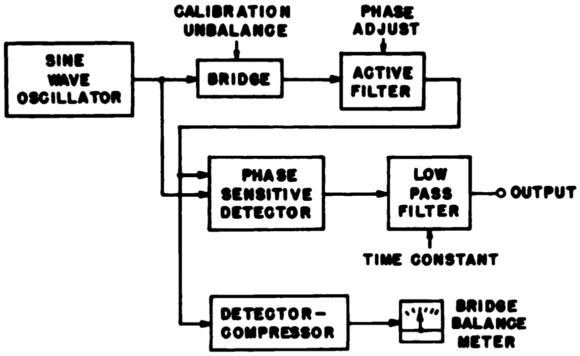

Fig. 1. Block diagram of the bridge

$$e_o/e_n = \frac{E}{4\sqrt{2kTBR_t}} \times (T.C.) \times \Delta T$$

This is more illuminating when the power dissipation in the thermistor is introduced. This is

$$P = \frac{(E/2)^2}{R_t}$$

Substituting in the equation above then gives

$$e_o/e_n = 1/2\sqrt{\frac{P}{2kTB}} \times (T.C.) \times \Delta T$$

Since this is independent of R_t, the thermistor can be selected to optimize the noise figure of the amplifier. A value on the order of 20kΩ to 200kΩ will result in a negligible noise contribution from modern solid-state amplifiers, and is consistent with thermistor fabrication capabilities.

The equation above relates signal change to the r.m.s. value of the noise. Usually the peak-to-peak value of noise, about six times greater, will be the more appropriate figure to use. Then the S/N ratio is about $(1/17)\ \sqrt{P/kTB}$ (T.C.) ΔT or, equivalently, the temperature change needed to give an output equal to peak-to-peak noise is

$$\Delta T = \frac{17}{(T.C.)}\sqrt{\frac{kTB}{P}}$$

With a $T.C.$ of 4% per degree Celsius, a thermistor power of 1 μW, a bandwidth of about 1.5 Hz (corresponding to a time constant of 0.1 s), and T near room temperature, the calculated value of ΔT is about 25×10^{-6} °C.

Stray capacitance of the thermistor and the cable appears in parallel with R_t and must be balanced to avoid overloading the synchronous detector; coarse- and fine-trimmer capacitors in parallel with R_1 serve this purpose. When the bridge is balanced, e_o has components having the origin in both the resistive and capacitive elements. Both components are out of phase with E, but they are always at 90° to each other. Therefore, when the reference phase to the synchronous detector is properly adjusted, it will be in phase with the resistive component while causing the capacitive component to be completely rejected, so that small changes in capacitance will not cause any output.

The frequency should be as low as possible to minimize the capacitive reactances, yet should be high enough to place the signal spectrum well out of the low-frequency noise region and to provide the desired bandwidth after filtering the second harmonic signal out of the detector. For this system a minimum time constant of 1 ms was desired, corresponding to a pass band of about 150 Hz. A modulation frequency of 500 Hz was selected to meet the above requirements.

Long-term stability depends on the stability of the bridge elements and stray admittances. Bridge resistors should have temperature coefficients of 2 or 3 ppm/°C near room temperature. Variable bridge resistors should consist of coarse and fine potentiometers, with the smallest total value that will accommodate the range of thermistor tolerances and temperature encountered. The calibrating resistors have so little effect that their tolerance is immaterial. For maximum long-term stability, the bridge, other than R_t could be placed in a temperature-controlled oven, although that was not done for this instrument.

High-resistance thermistors virtually eliminate trouble from series resistance, but shunt conductance, mainly in the cable to the thermistor, must be kept extremely low. Teflon insulation is ideal to take care of this. Good shielding is also essential, so that pick-up will not be high enough to cause overload before being rejected by the synchronous detector.

Several resistors and a pushbutton permit changing a bridge resistor the same fractional amount that R_t will change when heated 1×10^{-3} °C, assuming a temperature coefficient of −4% per degree Celsius for the thermistor.

With a 100kΩ thermistor that we used, the source resistance is 50kΩ. With this value, at 500 Hz, either bipolar or field effect transistors can have a noise figure of less than 2 db, so that the S/N ratio of the bridge, calculated above, will be essentially realized for the entire instrument; this is verified by test results. Our unit has a low-noise FET op amplifier, but if pick-up problems are severe, a lower value thermistor with a bipolar op amplifier might be better.

The bridge is direct coupled to the first amplifier stage with negative feedback to the fixed side of the bridge to set the sensitivity independent of thermistor value. Following this, the signal is ac coupled, further amplified, and band limited with an active filter. An L-C filter was found to be unsatisfactory because of a slight inductance shift with signal-level change as the bridge moves off balance. This resulted in an unwanted output signal if any capacitive unbalance existed, because of the resulting phase shift.

Synchronous detection is performed by a monolithic multiplier. This is another point of possible long-term drift. The effect of multiplier drift can be decreased at will by increasing the gain ahead of the multiplier, but this also decreases the range of signal and pickup that can be handled without overload, so that a low-drift multiplier is desirable.

Following the detector is a low-pass filter with switch-selectable time constants of 1, 10, or 100 ms, and a dc amplifier with gain switching in decade steps.

In addition, the unit includes a sine-wave oscillator, reference-phase-adjust network, test points, provision for monitoring bridge balance, etc. These are all routine features of a good lock-in amplifier, and will not be discussed in detail.

The Thermistor

The thermistors have been specially built for us by a commercial firm (*6*) with long experience (*2*) in the manufacturing of very quiet, stable thermistors. These units were beads made of copper oxide-free materials, hermetically sealed in glass and aged. Sizes of the final unit vary from 0.0125 cm to 0.025 cm. The leads are 25-μm nickel wires, attached to the platinum wire from the beads, with Teflon insulation. This is sealed with epoxy in the end of a 0.08 cm (o.d.) by 2.5 cm hypodermic stainless-steel tube. The nickel wire is then attached to 36-gauge copper leads and the whole encapsulated in a 0.25-cm stainless-steel tube. Figure 2 shows the thermistor unit as it is used in our thermal titration calorimeter (*7*). For most purposes a coating of polyvinylchloride over the stainless steel is adequate protection, but for blood work KEL-F dispersion (*8*) dip is applied, giving a 25–50 μm coating, free of pin-holes. Response times have been checked as described previously (*9*) and agree with our theoretical calculations. These run from 2.5 ms for the base units to 10–25 ms for the KEL-F coated units. Other coatings are under investigation that may be blood compatible and still have a fast response time. For the thermal titration unit, 0.1 s is adequate.

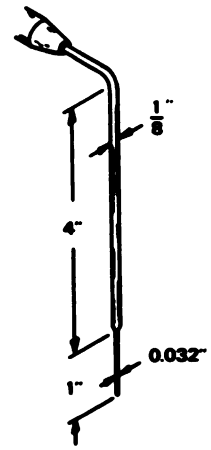

Fig. 2. Thermistor in stainless steel tube coated with KEL-F

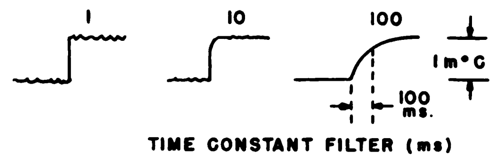

Fig. 3. Sensitivity and time response

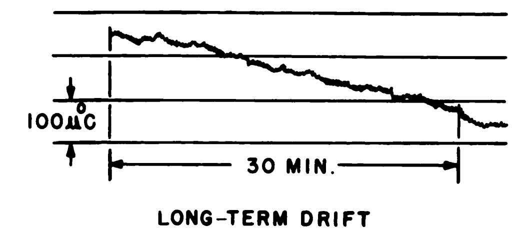

Fig. 4. Temperature drift

Experimental Procedure

The unit was tested in the lab with a 100kΩ, 0.01% precision resistor substituted for the thermistor. The resistor was connected to an 18-inch cable and enclosed in a styrofoam box. Output noise and drift were compared to the 1×10^{-3} °C calibration step caused by the pushbutton. The results are shown in Figure 3. The observed noise with the 100 ms time constant was about 25×10^{-6} °C peak-to-peak, as calculated, and it increased by a factor of about three with each factor of 10 decrease in time constant, as it should. The drift, after several hours warm-up, was about 1×10^{-6} °C/min, as shown in Figure 4, which was adequate for immediate requirements, and could probably be decreased if necessary, as discussed above. The main source is probably R_1, which consists of a 50kΩ precision resistor in series with 100kΩ and 10kΩ potentiometers with dial indicators. This is very convenient, as thermistors from 50kΩ to 160kΩ can be accommodated and the value of R_t can be read from the potentiometer dials. However, for the maximum stability, the adjustable portion of R_t should be much smaller.

Discussion

These figures are substantially better than those reported for other techniques. Platinum thermometers have a much lower temperature coefficient, giving a lower source signal-to-noise ratio, and require a much more elaborate sensing system to avoid serious additional degradation of S/N ratio. Thermocouples can easily attain better source S/N ratios than thermistors operated at the 1-μW level by getting the resistance down to a few ohms. However, the voltage is so low that it is not possible at present to amplify the signal without drastic decrease in S/N ratio. This is because the signal is dc, so that impedance transformation by a transformer is impossible unless the signal is chopped, and sufficiently low noise chopping is difficult. There is also the problem of temperature control of the reference junction and other junctions.

Transistor sensors have an inherent sensitivity of about 2 mV/°C, so the source S/N ratio depends on the equivalent input noise voltage. Unfortunately, this increases as frequency decreases, and operation other than dc is not attractive. A good low-noise transistor may have about 5 nV r.m.s./$\sqrt{Hz}$ equivalent input noise at 10 Hz. This is equivalent to about 15×10^{-6} °C peak-to-peak/$\sqrt{Hz}$, which is comparable to that of the thermistor, particularly for rapid measurements where more of the signal spectrum is at higher frequencies. However, it might be hard to incorporate a transistor in a suitable probe, and results reported to date indicate realization of only about 1×10^{-3} °C resolution at a power level of about 5 μW.

Reactive transducers are attractive because of their freedom from thermal noise with about the same ease of use as thermistors, as well as the possibilities of substantially shorter time constants (*3*). The S/N ratio theoretically attainable is proportional to Q (the ratio of peak stored energy to energy dissipated per cycle) of the device, and to the temperature coefficient of the capacitance. Unfortunately, for useful sensors fabricated so far, the latter has tended to be 10-fold lower than the *T.C.* of thermistors, thus largely offsetting the benefits resulting from the values of Q that have been achieved. In addition, the measurement circuitry is somewhat more complicated, and it can be anticipated that the practical difficulties in approaching the theoretical possibilities would be considerable, as has been the case with parametric op amplifiers.

Considering this brief review of alternatives, we think that the thermistor is probably the present device of choice for precision temperature measurement, although further confirmation of long-term stability is needed.

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