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A Four-Zone Furnace for Realization of Silver and Gold Freezing Points

D. C. Ripple, K. M. Garrity, and C. W. Meyer

National Institute of Standards and Technology, Gaithersburg, MD, USA 20899-8363

Abstract. Recently, the Thermocouple Calibration Laboratory at the National Institute of Standards and Technology has used sodium heat-pipe furnaces for the realization of ITS-90 freezing points of aluminum, silver, and gold. When using a fixed-point cell mounted in a long silica-glass tube that extends to ambient temperature at the top of the furnace, we have observed significant thermal gradients along the well of the fixed-point cell, with the top of the well up to 0.1 K colder than the bottom. Furthermore, the heat-pipe lifetime is limited when used at the gold point (1064.18 °C) for more than a few hundred hours. To address these problems, we have designed and built a four-zone furnace based on a temperature-controlled, graphite isothermal block, suspended inside a three-zone tube furnace. The three-zone furnace is of a commercial design. The graphite block is enclosed in an alloy 600 (Inconel) can, allowing the graphite to be maintained in an argon atmosphere. The argon pressure is maintained at one atmosphere at all temperatures, thereby greatly reducing the stress on the can. Heaters in intimate contact with the can allow temperature control of the fourth inner zone to high accuracy. In this paper, the measured thermal stability and uniformity achieved with this furnace are presented. We also give results of test freezes of a silver freezing-point cell.

INTRODUCTION

For the past eight years, the Thermocouple Calibration Laboratory at the National Institute of Standards and Technology has used sodium heat-pipe furnaces for the realization of ITS-90 freezing points of aluminum (660.323 °C), silver (961.78 °C), and gold (1064.18 °C). The fixed-point cells used in this laboratory are mounted in long silica-glass tubes that extend to ambient temperature at the top of the furnace [1]. By frosting the outer surface of the glass tube and by stacking several spaced graphite radiation shields above the fixed-point cell, heat transfer along the axis of the tube assembly is minimized and heat transfer in the radial dimension is maximized. Nonetheless, when these fixed-point cell assemblies are used in a sodium heat-pipe furnace, we have observed significant thermal gradients along the well of the fixed-point cell, with the top of the well up to 0.1 K colder than the bottom. Heat pipes themselves have excellent temperature uniformity [2,3]; the problem is thermal equilibration of the fixed-point cell and thermometer sheath with the heat pipe. The observed temperature nonuniformity can be substantially reduced by using a silica glass sleeve of a different design, but these changes were not practical for this laboratory. Additionally, the inner diameter of the heat pipes decreases when the heat pipe is operated at temperatures near 1064 °C for more than a few weeks, and there is an increased risk of the fixed-point cell assembly being seized in the heat pipe.

To address these problems, we have designed and built a four-zone furnace based on a temperature-controlled, graphite isothermal block that is suspended inside a three-zone tube furnace. The three-zone furnace is of a commercial design, with the temperature controlled using three type B thermocouples and proportional-integral-differential (PID) controllers. The graphite block is enclosed in an alloy 600 (Inconel*) can, allowing the graphite to be maintained in an argon atmosphere. The argon pressure is maintained at one atmosphere at all temperatures, thereby greatly reducing the stress on the alloy 600 can. Heaters in intimate contact with the can allow temperature control of the fourth inner zone to high accuracy. For this inner zone, a type S thermocouple is mounted adjacent to the heaters, and a nanovoltmeter is used as a preamplifier to the PID controller to reduce the noise of the control loop.

In this paper, we describe the design and construction of the furnace. Results for the measured thermal stability and uniformity of the constructed furnace are presented. We also present the results of sample freezes of a silver freezing point cell.

II. FURNACE DESIGN

The basic design of this furnace was motivated by the success at NIST with three-zone [4] and heat-pipe furnaces used in the NIST Platinum Resistance Thermometer Calibration Laboratory. The high temperature furnaces in this laboratory attain excellent temperature stability by using custom heaters in intimate contact with the outer wall of sodium heat pipes. The heaters are fabricated from wires of a proprietary nickel-chromium heater alloy (Chromel AA [5]) mounted in dual-bore alumina insulators. A control thermocouple is mounted between two of the alumina insulators. This arrangement gives much better response time than control thermocouples that are located some distance from relatively massive commercial heaters, with concommitant improvements in the stability of the temperature control loop. Unfortunately, operation near the gold freezing point requires a substantial power (greater than 1000 W), and heater lifetime may be limited.

Our new design retains the basic arrangement of the custom heater wrapped around a central core, but suspends the core in the bore of a larger three-zone tube furnace. This arrangement greatly reduces the power supplied by the core heaters. For use with fixed-point cells, the temperatures of the outer three zones can be held constant, and temperature control of only the core zone suffices to melt and freeze the metal in the fixed-point cell.

Tuning the set points of the outer three zones gives sufficient control of the thermal environment such that it is possible to use an isothermal block in the core instead of a heat pipe, which is both more expensive and is expected to have a shorter lifetime. By encasing the tube-shaped isothermal block in a closed sleeve of alloy 600 back-filled with argon, it is possible to use materials for the block that are reactive in air. A copper block would have excellent thermal conductivity, but its melting point is too low for confident reliability when used at the gold point. We chose graphite instead, which is inexpensive, reasonably high in thermal conductivity, and readily available in large sizes.

Our design parameters included the following requirements:

1. When setting a freeze, the block should cool at a rate of at least 0.1 K/min.
2. To allow prompt equilibration of the inner core, the 1/e settling time for the thermal profile of the insulation should be 10 min or less.
3. Thermal gradients from the furnace should be sufficiently attenuated in the block to maintain uniformity in the fixed-point cell of ±0.05 K over the length of the ingot well.

A schematic diagram of the furnace is shown in Figure 1. The heated length of the outer three zones in 0.6 m. Because a gap between the core assembly and the outer zones is desirable to promote radiative heating of the core assembly ends, the block length was chosen to be 0.53 m.

The response time of the block depends on the heat capacity of the block and the enclosed fixed-point assembly, and on the thermal resistance between the block and the outer three furnace zones. With a total mass of the core assembly of approximately 13 kg and insulation thicknesses of 2 cm, respectively, the 1/e equilibration time is approximately 55 min in the crude approximation that the block is fully surrounded by the insulation. In fact, the thermal coupling is significantly greater than the simple calculation: the top of the block is exposed; the alloy 600 support rods running through the insulation further circumvent the effectiveness of the insulation; the fixed-point cell has only graphite baffles inhibiting axial heat loss out of the block; and the block insulation, cut from slabs, has joints that allow passage of heat. When setting a freeze, the block should cool at a rate of approximately 0.5 K/min to ensure good nucleation of the solid phase of the freezing metal. This requires running the three-zone furnace at a temperature ΔT cooler than the block, with

$$\Delta T = (0.5\,\mathrm{K/min})\tau_{\mathrm{b}} \approx 30\,\mathrm{K}\,. \qquad (1)$$

For a fully insulated block, the predicted power loss in the block at this temperature difference is 60 W. In fact, we found that the response time of the actual furnace is approximately 20 min, with a corresponding increase in the steady-state power loss.

General guidance on the effectiveness of the graphite block at reducing thermal gradients can be obtained from a simple model that treats the cylindrical block wall as a plane slab of graphite adjacent to a plane slab of insulation. Assume that the outside boundary of the insulation has a slowly varying temperature profile $t_{\mathrm{i}}(x)$ in the plane of the slab, and that there is a net heating density varying as $q(x)$ at the interface between the graphite and

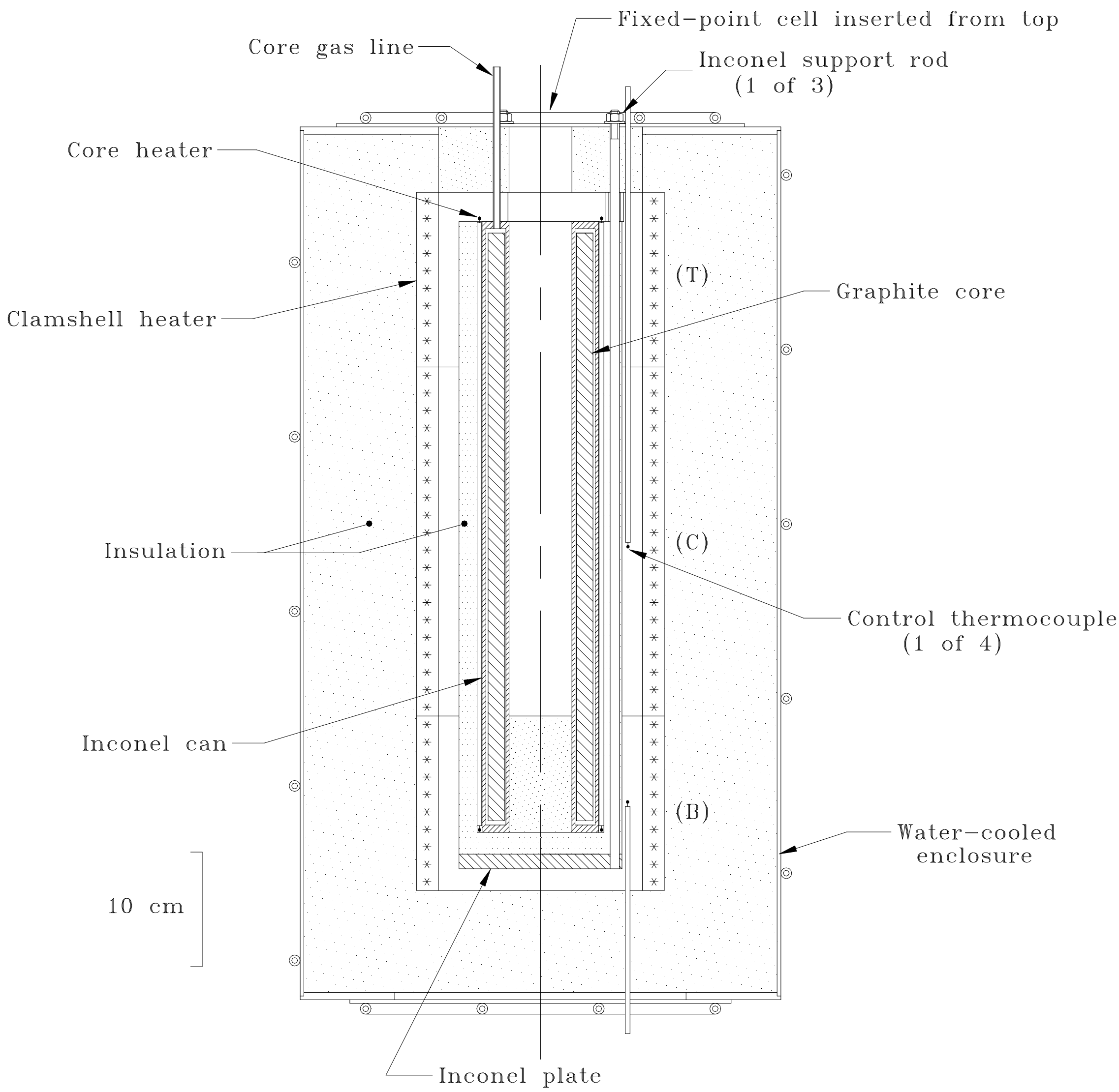

FIGURE 1. Schematic cross section of the four-zone furnace. The outer enclosure and heater wiring are not shown. (T), (C), and (B) indicate the top, center, and bottom zones, respectively.

the insulation. The equation for the temperature profile of the slab $t(x)$ is then:

$$\frac{d^2T}{dx^2} = -\frac{q}{A_b k_b} + \frac{(t-t_i)}{\alpha^2}, \qquad (2)$$

where A_b is the cross sectional area of the block, and

$$\alpha^2 = \frac{k_b}{k_i} s_b s_i , \qquad (3)$$

where k_b and k_i are the thermal conductivities and s_b and s_i are the thicknesses of the block and insulation, respectively. This equation can be solved for two cases: 1) variations in $t_i(x)$ induce gradients in the isothermal block profile, and 2) variations in $q(x)$ induce gradients in the block profile.

For case 1), we can express the temperature profile t_i as a Fourier series with amplitudes c_k for wave number k. The amplitude b_k of temperature modulations at wave number k induced in the isothermal block are

$$b_k = \frac{c_k}{1 + (\alpha k)^2} \quad . \qquad (4)$$

With s_i = 2.2 cm and s_b = 1.5 cm, α = 0.38 m. Recall that we are primarily concerned that the temperature be uniform over the 20 cm length of the freezing point ingot. Perturbations at a wavelength of 0.2 m (k=2π/(0.2 m) = 31.4 m^{-1}) are attenuated by a factor of 140. At longer wavelengths, the attenuation is not nearly as effective, but it will be possible to reduce long-distance nonuniformities in temperature by adjusting the set points of the three outer zones. The control points of the three outer zones are spaced 0.4 m apart. A 0.8 m wavelength is the maximum allowed with nodes at 0.4 m spacing: for this case, the attenuation $(b_k/c_k)^{-1} \approx 10$. Typical uniformities in a three-zone furnace are on the order of ±1 K, so an attenuation of 10 is near the limit of what is acceptable. The situation is not hopeless, however, because we have neglected the very significant attenuation of thermal fluctuations by the thermal conduction of the fixed-point cell itself.

A very similar expression describes the attenuation of temperature gradients in the block caused by variations in the net heat flux $q(x)$ along the length of the block. Although it is quite likely that there are large variations in $q(x)$ at the top and bottom of the block, the ingot of the freezing-point cell is placed in the middle of the core zone where $q(x)$ is expected to be nearly constant and the end effects are small.

The initiation of a freeze requires changes of fixed-point cell temperature and subsequent attainment of steady state over a period of approximately 20 min. Based on the diffusivity and geometry of the block and insulation, we have estimated the equilibration time for the establishment of steady-state thermal profiles in radial and axial directions of the core assembly. For the axial and radial directions, the 1/e equilibration times are approximately 7 min and 2 min, respectively.

CONSTRUCTION OF THE FURNACE

The outer three-zone furnace was a commercial product. We modified it simply by wrapping a water-cooled copper jacket around the furnace, thereby reducing heating of electronics inside the furnace cabinet, improving operator safety, and providing a uniform thermal boundary condition at the outside of the furnace.

The graphite core was machined from a single piece of high purity graphite into a tube shape of 9.1 cm outer diameter, 6.3 cm inner diameter, and 51 cm length. To reduce possible migration of carbon into the alloy 600 enclosure, the core was wrapped with a layer of woven silica-fiber tape. Then, the wrapped core was placed inside the alloy 600 enclosure and the top of the enclosure was permanently welded closed. The inner and outer cylinders of the alloy 600 enclosure are 3 mm thick. The top and bottom end caps are 6 mm thick. The heater surrounding the alloy 600 enclosure was fabricated by stringing lengths of 1.6 mm diameter Chromel AA heater wire into two-bore alumina tubes, and then welding the ends of the wire at the top and bottom of adjacent alumina tubes to form a serpentine heater. Electrical leads for the two semi-cylindrical heaters pass vertically through the top plate. The core and its surrounding insulation rest on a 1.3 cm thick alloy 600 plate, which is suspended from the top plate by three 0.8 cm diameter alloy 600 rods. The completed core assembly is readily removed from the outer furnace by simply lifting the top plate supporting the core.

ELECTRONICS FOR THE AG/AU FIXED-POINT FURNACE

All four zones of the furnace are heated with 60 Hz AC power. The outer three zones are driven directly by zero-crossing silicon-controlled rectifiers (SCRs) that control a supply voltage of 208 V AC. The top and bottom zones are rated at 5.1 A, 1160 W; the center zone is rated at 10 A, 2300 W. This amount of power is substantially higher than needed by the furnace for steady-state operation at the gold freezing point. The inner core heater has an impedance of only 7 Ω. To limit the power to the core and to better match the impedance of the AC wall circuits in our laboratory, a filament transformer of 2:5 ratio was inserted between a zero-crossing SCR that controls a 120 V supply voltage and the heater.

The temperatures of the three outer zones of the furnace are measured with type B thermocouples mounted in two-bore alumina insulators and inserted in an axial direction from the top or bottom of the furnace. We attempted to control the furnace with thermocouples inserted from the side of the furnace, but the thermocouples had insufficient immersion to give reliable control. The emf of each of these thermocouples is amplified with a commercial DC preamplifier and then connected to a simple proportional-integral controller.

Precise control of the core zone is critical for good regulation of the temperature of the fixed-point cell. For this zone, the type S thermocouple was first connected to an electronic ice-point compensator, and the compensated signal was fed into a DC nanovoltmeter. The analog output feature of the nanovoltmeter was used to generate an error signal proportional to the deviation of the thermocouple emf from a set point value, and this error signal is the input to a fourth proportional-integral controller.

Each of the four controllers uses digital, time-proportional pulses to control zero-crossing silicon-controlled rectifiers that, in turn, control the application of power to the heaters.

The furnace is protected from over temperature conditions of both the core temperature and the water-cooled jacket. If either location reaches an excessive temperature, a contactor controlling the main power opens.

FURNACE PERFORMANCE

The temperature profile along the well of the silver freezing-point cell is shown in Figure 2. These measurements were made with a Au/Pt thermocouple while the cell was approximately 2 K above the melting point of the silver. Because the DC preamplifiers have not been calibrated in absolute voltage units, the set-point values have been given in arbitrary units. Each set-point unit is approximately equal to 10 µV. As expected from the attenuation of short wavelength temperature fluctuations by the graphite block, the observed profiles vary smoothly with distance. A slight kink at –18 cm is apparent in a few of the curves. This position corresponds to the top level of the silver ingot, where there is a discontinuity in the thermal properties of the cell. With appropriate adjustment of the top and bottom set points, relative to the center-zone set point, we obtained a temperature profile that was uniform to ±0.03 K over the 20 cm length of the well (solid dots in Fig. 2). For thermocouple calibrations, this temperature homogeneity is adequate for high-quality fixed-point calibrations.

Figure 3 shows the typical response of the furnace when a freeze was initiated in a silver freezing-point cell. The freezing-point cell was maintained at a temperature approximately 2.5 K above its melting point overnight to fully melt the silver. At time zero, the core zone was taken off automatic control and the power reduced to 18 W. The core quickly cooled, at a maximum rate of –2 K/min, followed after a delay of approximately 6 min by cooling of the ingot at a maximum rate of –0.6 K/min. At 0.22 h, recalescence occured, and the emf measured by the type S thermocouple in the ingot rapidly rose to a plateau. The type S thermocouple was removed and a length of

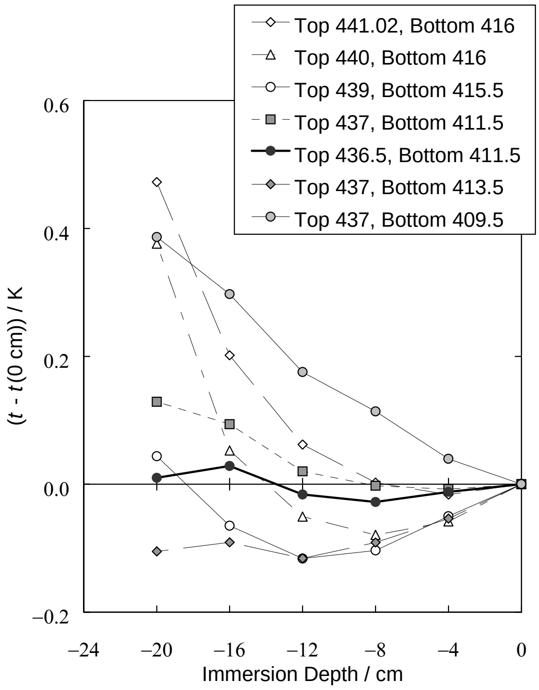

FIGURE 2. Immersion profiles in a silver freezing-point cell at a temperature 2 K above the freezing point, for a variety of furnace settings. For all profiles, the center zone was set at 417.5 (set point units approximately equal to 10 µV).

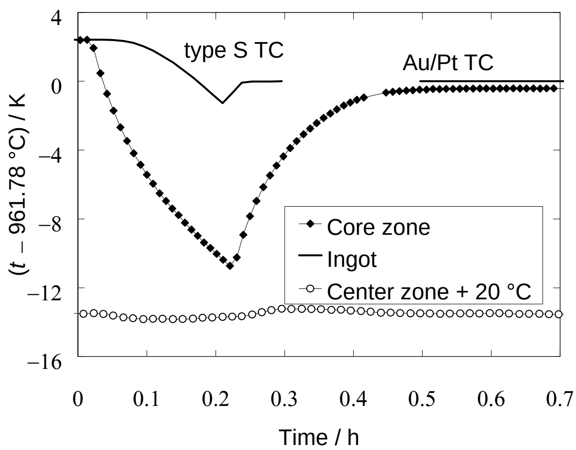

FIGURE 3. Temperature at full immersion in the well of the fixed-point cell ingot and of the center and core zones of the furnace during initiation of a freeze.

room-temperature alumina rod was quickly inserted into the fixed-point cell well to initiate an inner liquid-solid interface. After 2 min., the alumina rod was removed and a Au/Pt thermocouple was inserted into the well to monitor the full duration of the freeze. During the process of initiating the freeze, the large changes in power in the core have a slight effect on the

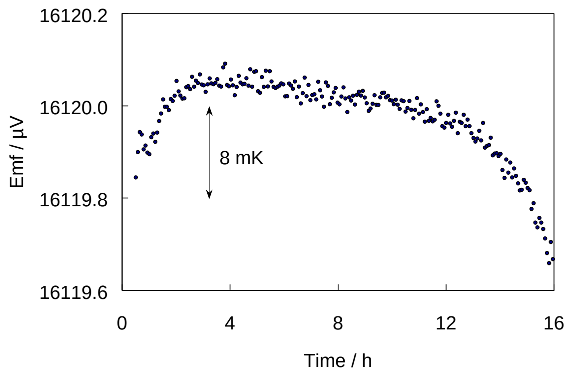

FIGURE 4. Freezing plateau of a silver freezing-point cell, as measured with a Au/Pt thermocouple.

temperature of the core zone, which initially cools below and then heats above its steady state value. These deviations of approximately 0.5 K were significantly smaller than the 33 K difference between the center and core zones during the freeze and did not significantly perturb the core zone or the freezing ingot.

The emf of the Au/Pt thermocouple measured during the freeze is shown in Fig. 4. Over a full 14 h, the emf of the thermocouple varied over a range of only 8 mK. This freeze duration is approximately twice as long as the freeze obtained in the sodium heat-pipe furnace of the NIST Thermocouple Calibration Laboratory. Prior to this measurement, the Au/Pt thermocouple had been quickly removed from the furnace at 962 °C. The initial rise in emf in the first 2 h of the freeze, equivalent to approximately 8 mK, was likely due to thermoelectric changes in the Au/Pt thermocouple as the thermocouple underwent annealing in the furnace. The data in Fig. 4 each represent 4 min averages and have an rms noise of 0.6 mK. This high precision is evidence that the heater windings of the furnace do not cause unacceptable noise in the thermocouple emf measurements.

Results similar to Figs. 3 and 4 have been obtained at the freezing point of gold. The performance of the furnace near the gold point is quantitatively very similar to the performance at the silver point.

CONCLUSIONS

We have demonstrated that this furnace design provides a sufficiently uniform thermal environment for successful measurements of thermocouples at the fixed points of silver and gold. The technique of maintaining the outer three zones at a constant temperature and only adjusting the core zone works well for fixed-point measurements.

Characterization of this furnace is not yet complete. In the near future, we intend to:

1. determine the lifetime of the core assembly,
2. determine the necessary interval for adjustment of the vertical uniformity of the furnace,
3. attempt to initiate freezes with a smaller temperature difference between the core and center furnace zones, and
4. determine if the outer three zones have sufficient stability when a DC preamplifier is not used with the control thermocouples.

ACKNOWLEDGMENTS

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REFERENCES

*Certain commercial equipment is identified in order to specify the experimental procedures. Such identification does not imply endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment identified is necessarily the best for the purpose.

1. Burns, G. W., and Scroger, M. G., *The Calibration of Thermocouples and Thermocouple Materials,* NIST SP250-35, U. S. Govt. Printing Office, Washington, 1989, pp. 200.
2. Neuer, G., and Brost, O., "Heat Pipes for the Realization of Isothermal Conditions at Temperature Reference Sources," in *Temperature Measurement 1975*, edited by B. F. Billing and T. J. Quinn, Inst. Phys. Conf. Ser. No. 26, Institute of Physics (UK), 1975, pp. 446-452.
3. Gotoh, M., and Hill, K. D., "Temperature Stability and Reproducibility of Pressure-Controlled Sodium-Filled Heat Pipe Furnaces," in *Temperature: Its Measurement and Control in Science and Industry*, Vol. 6, edited by J. F. Schooley, American Institute of Physics, New York, 1992, pp. 955-960.
4. Furukawa, G. T., *Journal of Research of the National Bureau of Standards-A. Physics and Chemistry* **78A**, 477-495 (1974).
5. Hoskins Manufacturing Co., Hamburg, MI, USA.