Journal of Glaciology, Vol. 22, No. 87, 1979

INSTRUMENTS AND METHODS

MERCURY-IN-GLASS THERMOMETERS FOR PRECISE TEMPERATURE MEASUREMENTS NEAR 0°C

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Abstract. Experience with the calibration and field use of mercury-in-glass calorimeter thermometers provides an indication of the accuracy attainable and the necessary corrections to obtain that accuracy. Secular changes as large as 57 mK have been observed during the first three years of thermometer use. Light physical tapping is found to reduce the thermometer readings by 3–6 mK. Corrections for variations in the external and internal bulb pressure and care to avoid parallax are necessary to obtain the best accuracy in field measurements. The best accuracy obtainable with these thermometers for temperature measurements near 0°C is approximately ±4 mK for laboratory measurements and ±5 mK for field measurements.

Résumé. *Thermomètres à mercure en verre pour mesures précises de températures au voisinage de 0°C.* Une expérience pour le calibrage et l'utilisation sur le terrain de thermomètres à mercure en verre donne des indications sur la précision accessible et les conditions nécessaires pour atteindre cette précision. Une variation séculaire de l'ordre de 57 mdeg a été observée au cours des trois premières années de l'utilisation d'un thermomètre. On constate que de petits tapotements réduisent l'indication du thermomètre de 3 à 6 mdeg. Des corrections en fonction des variations de pression externe et interne dans le réservoir du thermomètre et des soins pour éviter les erreurs de parallaxe sont nécessaires pour obtenir la meilleure précision dans les mesures de terrain. La meilleure précision accessible avec ces thermomètres pour mesurer des températures voisines de 0°C est approximativement de ±4 mdeg en laboratoire et de ±5 mdeg sur le terrain.

Zusammenfassung. *Quecksilber-Glasthermometer zur genauen Temperaturmessung um 0°C.* Erfahrungen mit der Eichung und dem Feldgebrauch von Quecksilber-Glasthermometern vermitteln einen Eindruck von der erreichbaren Genauigkeit und den notwendigen Korrekturen für eine solche Genauigkeit. Während der ersten drei Jahre des Thermometergebrauchs wurden säkulare Änderungen bis zu 57 Milligrad beobachtet. Beichtes Klopfen kann die Thermometerablösung um 3–6 Milligrad verringern. Korrekturen für Änderungen im äusseren und inneren Kugeldruck und Vermeidung von Parallaxen sind notwendig, um höchste Genauigkeit bei Feldmessungen zu erhalten. Mit diesen Thermometern lässt sich bei Messungen um 0°C eine maximale Genauigkeit von etwa ±4 Milligrad im Labor und von ±5 Milligrad im Feld erreichen.

Introduction

Some glaciological problems require temperature measurements near the ice-point (IP) to accuracies of 10 mK or better. Such measurements can be difficult and expensive. Examples are laboratory measurements of the freezing-point depressions of dilute aqueous solutions and field measurements of supercooled water temperatures in rivers. Mercury-in-glass calorimeter thermometers offer a relatively simple, cheap, reliable, and accurate means for determining these temperatures. This paper reviews experience with the calibration and field use of four such thermometers.

The thermometer scale ranges from +1 to −1°C over a length of *c.* 250 mm. The smallest scale division is 5 mK. An expansion chamber is provided at the top of the capillary bore. The bulb is 70 mm in length and 7 mm in diameter. These thermometers can be read to a precision of about 2–3 mK without a magnifier.

Calibration

All calibrations were carried out in IP cells or in triple-point (TP) cells. The TP of water is defined as +0.010 0°C and this temperature can be reproduced to 5×10^{-5} K (Beattie and others, 1938), which is much smaller than the sensitivity of the thermometers. Consequently, no calibration corrections were applied to the TP cell temperatures. The temperature T, in °C, in an IP cell at a distance h in mm below the surface of the water is, according to Beattie and others (1937)

$$T = -1.32\times10^{-5}(P-760)-7.2\times10^{-7}h-55(K-0.7\times10^{-6}), \qquad (1)$$

https://doi.org/10.3189/S0022143000014350 Published online by Cambridge University Press

where K is the specific electrical conductance of the water in the cell in units of $\mu S\ cm^{-1}$ measured at 0°C. It is assumed that the water used in preparing the cell has been saturated with air at 0°C and a barometric pressure of P in mm of mercury. The IP cells used in the calibrations were prepared from ice cubes of de-ionized water which were ground into fine ice with a commercial blender. The ice was packed into a one-liter Dewar, although in a few cases a four-liter Dewar was used. De-ionized water was added until the ice floated and then the excess water was decanted and more ice was added to the Dewar. Special care was taken to clean all containers and utensils to prevent contamination of the cells. The IP cells were allowed to stand for *c.* 1 h to equilibrate before use. In some cases, barometric pressure at the time of calibration was measured. In most cases, when the calibration was completed a sample of a few milliliters of water was withdrawn and its electrical conductivity measured. These conductivities averaged 4 $\mu S\ cm^{-1}$ at 0°C. Using Equation (1), the temperature in the IP cells was estimated to be 0°C ± 1 mK.

Thermometer corrections included an emergent-stem correction and a correction for variations in the external bulb pressure caused by changes in atmospheric pressure. The emergent-stem correction (Wise, 1976) for the thermometers was always less than 1 mK for both TP and IP calibrations. Corrections for changes in pressure were estimated using a pressure coefficient of 0.1 K $atmos^{-1}$ (Wise, 1976). In the cases where pressure was measured, these corrections were *c.* ±1 mK. Some of the above calibrations and thermometer corrections are compensatory and it is estimated that these corrections never exceeded ±3 mK for all the calibrations.

The difference between the observed temperature T_0 and the calibration temperature T is $T_0 - T = \Delta T$. The variations of ΔT with time are a measure of the secular changes of the thermometers and are shown in Figure 1. Thermometers 4 and 5 had large secular changes during their first three years of use (52 and 57 mK) but now appear to be stabilizing. The secular changes in thermometers 1 and 2 are smaller and also appear to be stabilizing. It is clear that these secular changes must be taken into account for precise temperature measurements.

In September 1974 it was found that the thermometer readings could be changed by tapping the thermometers very lightly against the bottom of the Dewar. Experimentation showed that tapping could reduce the thermometer readings by 3–6 mK and that a very light

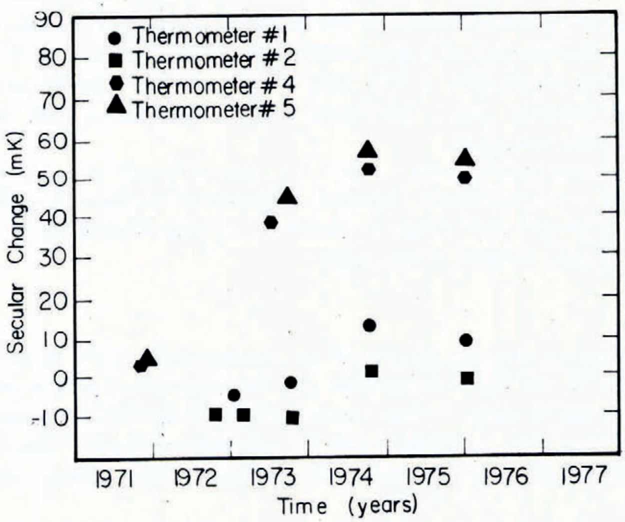

Fig. 1. Secular change versus time for thermometers 1, 2, 4, and 5. The secular change, $\Delta T = T_0 - T$, where T_0 is the observed temperature and T is the calibration temperature.

https://doi.org/10.3189/S0022143000014350 Published online by Cambridge University Press

blow produced the changes (e.g. a drop of 1–2 mm on the bottom of the Dewar or light tapping with a pencil). This effect appears to be caused by erratic motion of the mercury column in the very fine capillaries required in these thermometers (Hall and Leaver, 1962).

Table I presents data for a series of TP and IP calibrations carried out in September and October 1974. The standard deviations for each thermometer are given in parentheses; they range over 2 to 4 mK for all the calibrations. Another measure of the thermometer accuracy is the difference in the values for the TP and IP calibrations, in principle 10 mK. These differences ranged from 11–14 mK for the average values of the TP and IP calibrations. The last column in Table I shows the differences between the TP and IP calibrations for each thermometer on one day, 10–11 mK. It appears that these four thermometers, under the conditions of use described, can reproduce the IP and TP temperatures to about ±4 mK. This value represents the best accuracy attainable for temperature measurements near 0°C.

TABLE I. CALIBRATION DATA FOR THERMOMETERS 1, 2, 4, AND 5 FOR SEPTEMBER AND OCTOBER 1974 (in °C)

Thermometer	*Triple-point (September 1974)*	*Ice-point (September–October 1974)*	*Difference*	*Difference for 25 September 1974*
1	+0.025 (±0.003)	+0.012 (±0.003)	+0.013	+0.010
2	+0.014 (±0.002)	0.000 (±0.003)	+0.014	+0.011
4	+0.063 (±0.004)	+0.052 (±0.002)	+0.011	+0.010
5	+0.068 (±0.003)	+0.056 (±0.002)	+0.012	+0.010

FIELD USE

When the thermometers were used in the field, they were calibrated periodically in the laboratory with TP or IP cells and then transported to the field site. For some applications it may be desirable to do the TP or IP calibrations at the field site. Calibration corrections are not required when using TP cells, however, certain situations may require calibration corrections for even carefully prepared IP cells. For example, if the laboratory and field site are at high elevation or if the laboratory and field site are separated by a large altitude difference, the pressure correction may become significant. Equation (1) predicts a change of *c.* 1 mK for a change in elevation of 1 km (from sea-level).

The most significant thermometer corrections in the field are secular changes, changes produced by variations in bulb pressure, and the effects of parallax on the readings. Secular changes, such as those shown in Figure 1, were taken into account by frequent calibrations in the TP or IP cells. Changes in bulb pressure can be external or internal. Such changes were evaluated using Wise's (1976) value of the pressure coefficient, 0.1 K atmos^{-1}. A change of external or internal pressure of 10 mm of mercury can produce a change of *c.* 1.3 mK in the thermometer reading. This pressure variation can be produced by a change in elevation of *c.* 106 m from sea-level, the passage of weather fronts, or tilting the thermometer from the vertical position when the reading is taken (assuming the thermometer was calibrated in the vertical position). Laboratory experience has shown that if care is not taken with the readings, parallax may produce errors of a few mK. The required corrections can be substantial in certain cases. For example, a 20 mm of mercury increase in barometric pressure coupled with tilting the thermometer 45° from the vertical would require a correction of *c.* 9 mK to the reading. It is estimated that the best accuracy obtainable in the field with these thermometers for measurements near 0°C is about ±5 mK and that this level of accuracy requires careful consideration of the factors cited herein.

ACKNOWLEDGEMENTS

This research was partially supported by the Earth Science Section, National Science Foundation, NSF Grant GA-30748. I wish to thank Mr R. E. Gilfilian for his help with the laboratory and field measurements. The final draft of this manuscript was prepared while I was on leave at the U.S. Army CRREL, Hanover, N.H., U.S.A. and I wish to thank the personnel there for making their facilities available to me.

MS. received 7 August 1978

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