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U.S. DEPARTMENT OF COMMERCE/Technology Administration
National Institute of Standards and Technology

Standard Reference Materials:

Standard Reference Material 1747: Tin Freezing-Point Cell and Standard Reference Material 1748: Zinc Freezing-Point Cell.

Gregory F. Strouse and Ahmet T. Ince

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Standard Reference Material 1747: Tin Freezing-Point Cell and Standard Reference Material 1748: Zinc Freezing-Point Cell

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Abstract

The freezing points of Sn (231.928 °C) and Zn (419.527 °C) are defining fixed points of the International Temperature Scale of 1990 (ITS-90). Realization of these freezing points is performed using fixed-point cells containing high-purity (≥99.9999% pure) metal. The five Sn and five Zn freezing-point cells constituting Standard Reference Material (SRM) 1747 and SRM 1748, respectively, have been constructed and certified as suitable for use in the realization of the freezing-point temperatures of Sn and Zn for the ITS-90. The expanded uncertainties (k=2) assigned to the freezing-point temperatures of the fixed-point cells SRM 1747 and SRM 1748 do not exceed 0.40 m°C and 1.1_4 m°C, respectively. In this document, the methods used for the construction of the SRM Sn and SRM Zn freezing-point cells and their certification are described.

Disclaimer

Certain commercial equipment, instruments or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Acknowledgment

The authors wish to thank the Standard Reference Materials Program for their support in the development of these new SRMs and William Guthrie of the Statistical Engineering Division for his helpful discussions on uncertainties.

1. Introduction

The two freezing points required to realize the International Temperature Scale of 1990 (ITS-90) from 0 °C to 420 °C are that of Sn (231.928 °C) and Zn (419.527 °C)[1]. These freezing points are realized by using thermometric fixed-point cells containing high-purity (≥99.9999% pure) metals. Sn and Zn freezing-point cells, with the triple point of water (TPW) cell (0.01 °C), are used for the ITS-90 calibration of standard platinum resistance thermometers (SPRTs) from 0 °C to 419.527 °C, for part of the calibration of SPRTs from 0 °C to 660.323 °C, and for part of the calibration of high-temperature SPRTs (HTSPRTS) from 0 °C to 961.78 °C. To provide certified fixed-point cells for this purpose, we have developed two Standard Reference Materials (SRMs), the Sn Freezing-Point Cell (SRM 1747) and the Zn Freezing-Point Cell (SRM 1748).

Five fixed-point cells of each type (designated Sn 95-1, Sn 95-2, Sn 95-3, Sn 95-4 and Sn 95-5; Zn 95-1, Zn 95-2, Zn 95-3, Zn 95-4 and Zn 95-5) were certified as SRMs. The certification procedure of each cell included the evaluation of freezing and melting curves and the direct comparison with the appropriate laboratory freezing-point standard (Sn 88A or Zn 93-4) in the NIST Platinum Resistance Thermometry (PRT) Laboratory. Four of each of the five cells were selected as SRMs available through the Standard Reference Materials Program with the fifth cell (Sn 95-1 and Zn 95-4) kept in the NIST Platinum Resistance Thermometer Laboratory as an SRM reference cell. The certification procedure and results of the two SRMs are given below.

2. Samples and Filling Procedure of the SRM Freezing-Point Cells

2.1 SRM samples

A 6 kg lot (M3821) of high-purity (≥99.9999% pure) Sn metal to be used for SRM 1747 and a 6 kg lot (M3371) of high-purity (≥99.9999% pure) Zn metal to be used for SRM 1748 were purchased from Johnson Matthey Company of Spokane, Washington. The metals were in teardrop form (nominally 3 mm o.d.) placed in plastic bottles, each containing 1 kg of Sn or Zn sealed in an Ar atmosphere. The Johnson Matthey Company emission spectrographic assay of the Sn (Appendix A) shows the total impurity level to be 0.6 μg/g (0.6 parts per million), resulting from 0.3 μg/g of Sb, 0.2 μg/g of Bi and 0.1 μg/g of Ag; and the emission spectrographic assay of the Zn (Appendix B) shows the total impurity level to be 0.3 μg/g (0.3 parts per million), resulting from 0.2 μg/g of Sn and 0.1 μg/g of Cu.

2.2 SRM freezing-point cell specifications and design

Five thermometric fixed-point cells of each metal were constructed for certification as ITS-90 freezing-point standards. Each SRM 1747 cell contains 1071 g of the high-purity Sn metal from randomly selected bottles of lot M3821 and each SRM 1748 cell contains 1031 g of the high-purity Zn metal from randomly selected bottles of lot M3371.

As shown in figure 1, the metal (K) was contained within a high-purity graphite crucible (L), with a high-purity graphite cap (I) and a high-purity graphite re-entrant well (J). The graphite assembly was placed inside a precision-bore borosilicate-glass envelope (H) (46.2 cm long, ground to 5 cm o.d. with a wall thickness of 0.4 cm). Axially located in the annular space between the graphite crucible and the borosilicate-glass envelope was a piece of ceramic fiber blanket (M) (24.3 cm long, 14.1 cm wide and 0.15 cm thick) for thermal insulation between the borosilicate-glass envelope and the graphite crucible and to provide cushioning for the graphite assembly. Above the graphite cap, there was a matte-finished borosilicate-glass guide tube (F) (1.0 cm o.d. with a wall thickness of 0.1 cm), 1.2 cm thick washed-ceramic fiber disks (E) and two graphite heat shunts (G). The first heat shunt was placed approximately 3.2 cm and the second heat shunt was placed approximately 10.8 cm above the top of the graphite cap and are snug fitting in the borosilicate-glass envelope. A space of about 1.8 cm between the top of the borosilicate-glass envelope and the ceramic fiber insulation allows for the silicone rubber stopper to be glued into place using silicone-rubber sealant in the top of the borosilicate-glass envelope. This silicone rubber stopper (D) has (1) a modified compression fitting with a silicone rubber O-ring (C) for inserting and sealing the SPRT into the fixed-point cell and (2) a stainless steel gas filling tube (B) (4.3 cm long and 0.3 cm o.d.) for evacuating and backfilling the cell with an inert gas. Additionally, the gas filling tube allows for a slight overpressure (0.25 kPa above atmospheric pressure) of an inert gas (Ar or He) in the cell to prevent contamination of the metal.

The immersion depth for the SRM cells was 18 cm from the sensor mid-point of the SPRT to the top of the liquid metal surface (distance from the bottom of the graphite re-entrant well to the top of the liquid level is 20.5 cm). The pressure in the cells during use was 101 325 Pa ±27 Pa.

The high-purity (≥99.9999% pure) graphite pieces (crucible, well, cap and heat shunts) used for SRMs 1747 and 1748 were purchased from Carbone of America, Ultra Carbon Division, Bay City, Michigan. The usable volume space, allowing for a 1 cm head space between the liquid metal and the underside of the graphite top, is 149 cm^3.

The fixed-point cell assembly of the Sn and Zn freezing-point cells was placed inside a three-zone furnace for evaluation. A description of the furnace may be found in Ref. [2].

2.3 Filling of the SRM freezing-point cells

Any handling procedure of high-purity material is apt to introduce contamination. The teardrop form is convenient for handling and filling during freezing-point cell construction, while a solid cylindrical sample may require cutting and cleaning. By using one-time use polyethylene gloves, efforts were made to maintain the purity of the metal and the fixed-point cell components that come in contact with the metal.

Prior to filling the graphite crucible with the metal sample, the graphite crucible assembly (crucible, cap, re-entrant well) and graphite heat shunts were placed in a silica-glass furnace tube and "baked-out" at 650 °C under vacuum for 4 hours. This "bake-out" of the graphite was a final purification

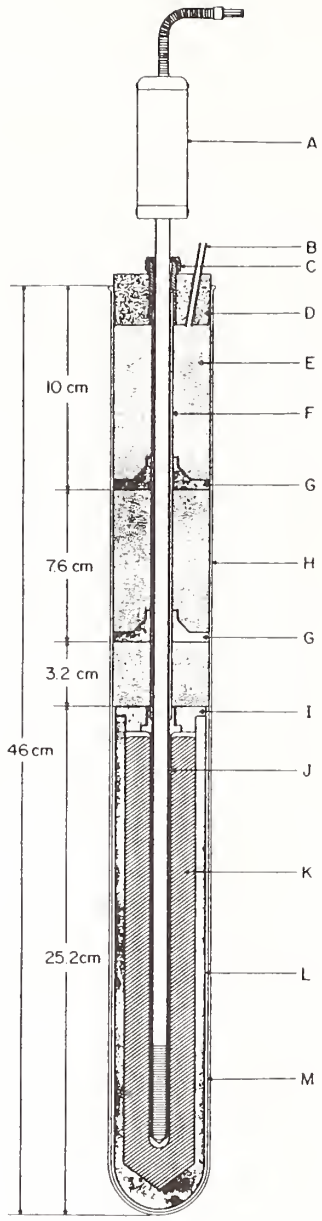

Figure 1. A schematic of an SRM freezing-point cell showing: (A) a 25.5 Ω SPRT; (B) fill tube to inert gas (Ar or He) supply and pressure gauge; (C) thermometer gas seal (a modified Swagelok fitting with a silicone rubber O-ring); (D) silicone rubber stopper; (E) thermal insulation (1.2 cm thick washed Fiberfrax disks); (F) matte-finished borosilicate-glass guide tube; (G) two graphite heat shunts; (H) precision-bore borosilicate-glass envelope; (I) graphite cap; (J) graphite re-entrant well; (K) metal sample; (L) graphite crucible; (M) thermal insulation between the borosilicate-glass envelope and the graphite crucible.

to remove hydrocarbons and other contaminants that might have been present from the fabrication process. The vacuum system used in the fabrication of the freezing-point cells is described in Ref. [2].

After the graphite assembly was heated and then cooled to ambient temperature under vacuum, the furnace tube was purged with purified Ar gas and the graphite pieces removed and placed inside a clean polyethylene bag for storage. To remove any contaminants from the "bake-out," the silica-glass furnace tube was (1) cleaned in hot, soapy water; (2) rinsed with copious amounts of water; (3) the inside soaked in 20% nitric acid-80% distilled water (volume) for 2 hours; (4) rinsed with copious amounts of distilled water and then (5) dried. The silica-glass furnace tube was cleaned after each use ("bake-out" or "fill").

In order to introduce 1071 g of Sn or 1031 g of Zn into the crucible and insert the graphite re-entrant well, two fillings were required. Approximately, 760 g of Sn or 800 g of Zn could be poured directly into the graphite crucible for the first "fill." The graphite crucible with the graphite cap containing the appropriate metal sample was placed into the cleaned furnace tube and the furnace tube was placed in the furnace. The system was evacuated for 1 hour and then back-filled with purified Ar to a pressure of about 34 kPa. This process of pumping and flushing the system was carried out three times, with the system finally under vacuum. For Sn, the furnace was turned on and the temperature was brought to 235 °C to melt the sample. For Zn, the furnace was turned on and the temperature was brought to 424 °C to melt the sample. When the Zn metal reached a temperature of about 345 °C, the vapor pressure of the Zn was high enough to cause vapor deposition of the Zn on the inner wall of the furnace tube. To prevent that vapor deposition, the furnace tube was backfilled to a partial pressure of about 34 kPa of purified Ar. After about 3 hours, the sample was completely melted and the furnace was then allowed to cool to ambient temperature before removal of the graphite crucible from the furnace tube.

For the second "fill," the remaining metal was added to metal in the graphite crucible from the first "fill." The graphite re-entrant well was inserted in the graphite crucible as far as possible through the hole in the graphite cap and the assembly was placed in the newly cleaned furnace tube. A silica-glass push rod extended from the bottom of the graphite re-entrant well through a vacuum seal at the top of the furnace tube and for a sufficient distance above the seal at the top of the furnace tube to allow the graphite well to be pushed into place when the metal was molten. Finally, using the method described above, the furnace tube was placed in the furnace and pumped and flushed with purified Ar and the metal sample was melted. When the sample had melted, the graphite re-entrant well was slowly inserted into the molten metal by pushing down the silica-glass push rod. When the graphite well was fully inserted, the furnace was turned off, the system allowed to cool to ambient temperature, and the filled graphite crucible assembly removed and placed inside a clean polyethylene bag for storage. The filled graphite crucible assembly was then placed into its borosilicate-glass envelope and fixed-point cell assembly that was described earlier.

3. Certification Procedure for SRM 1747 and SRM 1748

The first step in certifying the fixed-point cells was to obtain three freezing and three melting curves for each of the specimens in the cells, using a 25.5 Ω standard platinum resistance thermometer (SPRT). The second step in certifying the fixed point cells was to obtain three direct comparisons with the appropriate laboratory standard by simultaneously freezing both the SRM cell and laboratory standard. An Automatic System Laboratories (ASL) F18 30 Hz ac resistance ratio bridge, with a thermostatically controlled (25 °C ±0.01 °C) Tinsley 5685A ac/dc 100 Ω reference resistor, was used to measure the SPRT. A description of the measurement system used in the PRT Laboratory may be found in Ref 3.

3.1 Freezing-point realization

In the realization of the freezing point, the recommended "induced inner freeze" method [4,5] was used. Due to the deep supercool of approximately 25 K below the freezing-point temperature of high-purity Sn, the technique for the realization of the Sn freezing point is different from that of the other ITS-90 freezing-point metals. The freezing point was achieved by heating the cell overnight to approximately 5 K above the freezing-point temperature and then setting the furnace temperature about 0.5 K below the freezing-point temperature of the metal and monitoring the temperature of the metal with the check thermometer. When the Sn had cooled to its freezing-point temperature, the freezing-point cell with the check thermometer was removed from the furnace until the start of recalescence. At the beginning of that recalescence, the fixed-point cell was placed back into the furnace, the check thermometer removed and two fused-silica glass rods were inserted three minutes each into the reentrant well of the cell to induce an inner solid-liquid interface.

The freezing point of Zn was achieved by heating the cell overnight to approximately 5 K above the freezing point temperature and then setting the furnace temperature about 1 K below the freezing-point temperature of the metal and monitoring the fixed point with the check thermometer during the supercool of the metal and the subsequent recalescence. At the beginning of the recalescence, the furnace control temperature was set to approximately 0.5 K below the fixed-point temperature of the metal, the check thermometer removed and two fused-silica glass rods were inserted five minutes each into the reentrant well of the cell to induce an inner solid-liquid interface.

Finally, for both the Sn and Zn SRM cells, the "cold" thermometer was reinserted into the cell and, after equilibrium was obtained, measurements begun. Using an excitation current of 1 mA, thermometer readings were recorded continuously until the freezing was complete. After each freezing-point realization the SPRT was measured at the TPW to ensure that the thermometer had not changed.

From the analysis of the freezing curve plateaus, an estimation of the total impurity level in the metal sample may be made using Raoult's Law of dilute solutions [6]. The total impurity level obtained from the assay of the metal sample and Raoult's Law of dilute solutions gives a calculated estimation of the depression in temperature over the first 50% of a freezing curve. The calculated and the

experimentally determined temperature depressions may be compared to confirm the overall purity of the metal sample in the fixed-point cell. Differences between the calculated and the experimentally determined temperature depressions may indicate either that Raoult's Law of dilute solutions is not exact, that the sample contained additional impurities not accounted for in the emission spectrographic assay or perhaps that additional impurities were inadvertently added to the metal during the construction of the fixed-point cells. In estimating the expected temperature depression, Raoult's Law of dilute solutions is intended to provide a guideline and does not strictly apply. Additionally, there is an uncertainty in the extrapolation method chosen to derive the temperature depression.

3.2 Melting-point realization

After the metal sample was slowly and completely frozen in the above manner, the furnace temperature was set at about 1 °C above the freezing-point temperature to slowly melt the metal over a time of approximately 10 hours. Using an excitation current of 1 mA, thermometer readings were recorded continuously until the melting was complete. After each melting-point realization, the SPRT was measured at the TPW to ensure that the thermometer had not changed.

The temperature range of a melting curve is not indicative of the purity of the metal. Using the melting curve to indicate purity is complicated by the fact that the shape and range of a melting curve will depend upon the history of the previous freezing of the metal in the fixed-point cell [7]. A slow freeze ($\geq$10 h) causes the impurities to be segregated, which in turn causes a large melting range. A fast freeze (<30 min) causes a homogenous mixture of the impurities within the metal sample, which in turn causes a small melting range. A fast freeze is realized by removing the fixed-point cell to ambient and allowing the molten metal to quench freeze.

During the melting of the sample, two liquid-solid interfaces are formed. One liquid-solid interface is next to the inner wall of the graphite crucible and the second liquid-solid interface is near the graphite re-entrant well. This second liquid-solid interface is formed where the lower-purity metal solidified at the end of the previous slow freeze. The lower-purity metal has a slightly lower freezing and melting temperature causing this second liquid-solid interface to form during the melt. Analysis of the freezing and melting curves, shows that their temperature ranges are about the same, which is expected if an inner melt is formed during the melt [8].

3.3 Direct comparison measurements

The second part of the certification was a direct comparison of the fixed-point cells under test with the laboratory standard fixed-point cell to determine their freezing-point temperatures relative to that of the reference cell. The five SRM Sn cells and five SRM Zn cells were directly intercompared with the NIST laboratory reference cells Sn 88A and Zn 93-4, respectively. This was obtained by realizing simultaneous freezes for the two cells in two separate but identical furnaces and making three sets of alternate measurements, at equal time intervals, on their freezing-curve plateaus, using an SPRT. This ensures that the comparison measurements on the two cells were made at

approximately the same liquid-solid ratio of the metal samples. Ideally, the equivalent temperature difference between measurements of each of the pairs would be identical. However, due to small differences in sample purity, only the first of the three pairs of measurements on the cells was used for the comparison. The other two pairs of measurements on the cells provided information on the progress of the freezes. The fraction of metal frozen during a set of three measurements of the freezing-point temperature of each cell did not exceed 20%. The SPRT was measured with excitation currents of 1 mA and 1.414 mA to permit extrapolation to zero-power dissipation (0 mA). Corrections were made for any differences in pressure and hydrostatic head effects in each cell. Each cell was measured using an SPRT three times during the direct comparison and this procedure was repeated two times. Following each set of direct comparison measurements, the SPRT was measured at the TPW to ensure that the thermometer had not changed.

For the metal to be certified as a freezing-point standard, the fixed-point cells containing samples of the metal should have a freezing-point temperature that is in agreement with the laboratory reference cell containing high-purity metal to within the uncertainties of the measurements. If the purity of the metal in the new fixed-point cell is greater than that of the reference cell, then it may be of even higher quality, as indicated by being "hotter" than the laboratory standard. A cell that is "hotter" usually has fewer impurities, since impurities in these samples will usually decrease the freezing-point temperature.

4. **Analysis of Results**

4.1 Analysis of SRM freezing-point curves

Figures 2 to 6 show the freezing curves for each of the five Sn fixed-point cells and figures 7 to 11 show the freezing curves for each of the five Zn fixed-point cells (the region of supercooling and recalescence are not shown, as the curves begin after the reinsertion of the thermometer). Using an excitation current of 1 mA, thermometer readings were recorded continuously until the freezing was complete. The average length of a freeze for the five Sn cells was 10 hours and it was 12 hours for the five Zn cells. The time-temperature relationship shown in the figures are calculated from the change in resistance of the SPRT during a freezing-point realization. For comparison purposes, the three freezing curves for each cell shown the figures were normalized so that the maximum SPRT resistance obtained during the freezing-point realization is equivalent to the 0 m°C point on the graph. The calculated temperature depression when 50% of the metal was frozen and the shapes from the freezing-curve plateaus were used to estimate and confirm the overall purity of the sample in the cell.

In most cases, impurities present in the high-purity samples will cause a depression in the temperature of a freezing point. The total mole fraction impurity level of the metal sample (7.5×10^{-7} mol for Sn and 4.6×10^{-7} mol for Zn) and Raoult's Law of dilute solutions give a calculated estimation of the depression in temperature of 0.2 m°C for Sn and 0.3 m°C for Zn. As experimentally determined from the freezing curve plateaus in figures 2 to 6, the average estimated temperature depression from the extrapolated 0% frozen metal (time of recalescence) to the 50%

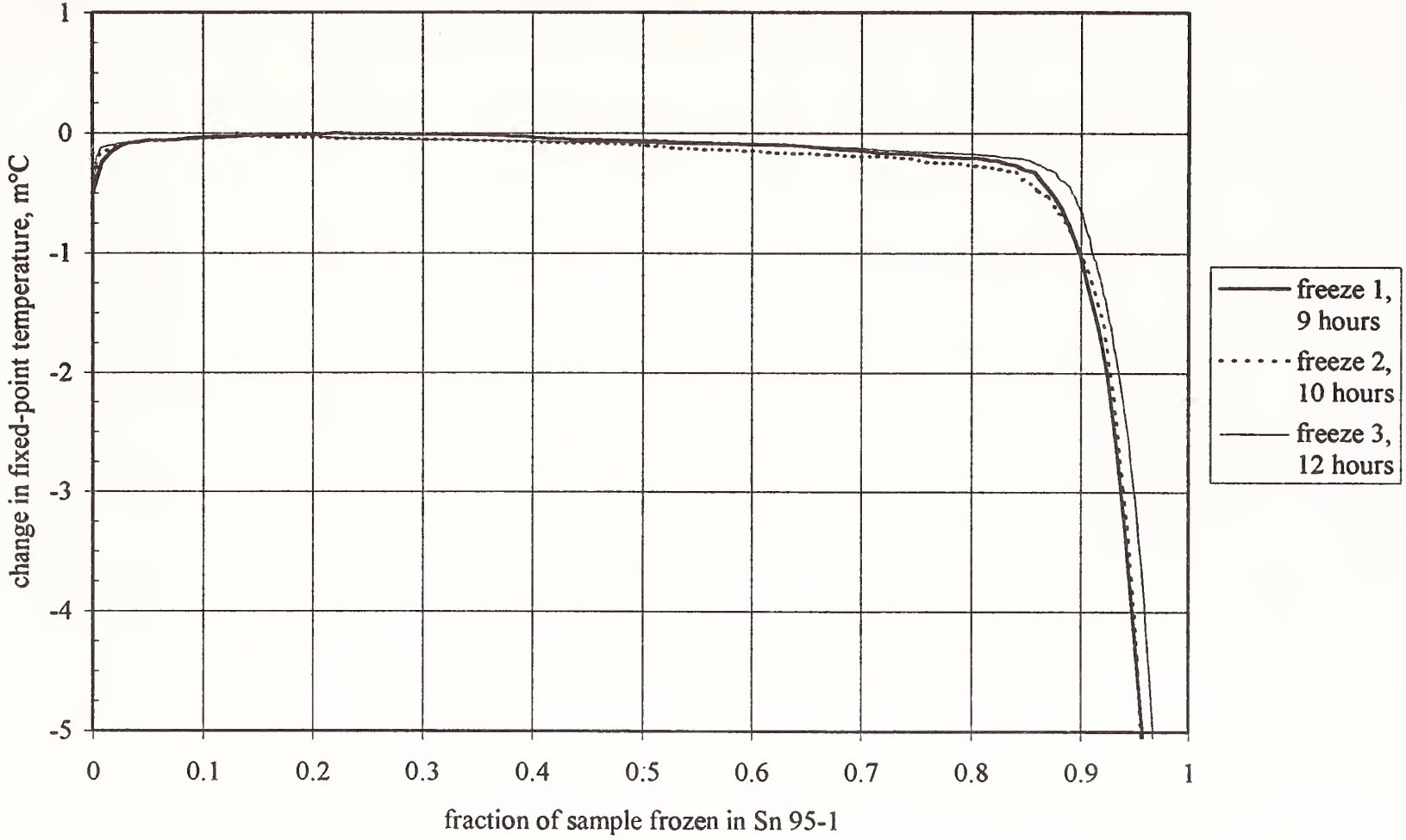

Figure 2. Three freezing curves for the SRM 1747 fixed-point cell Sn 95-1 using the "induced inner freeze" preparation technique.

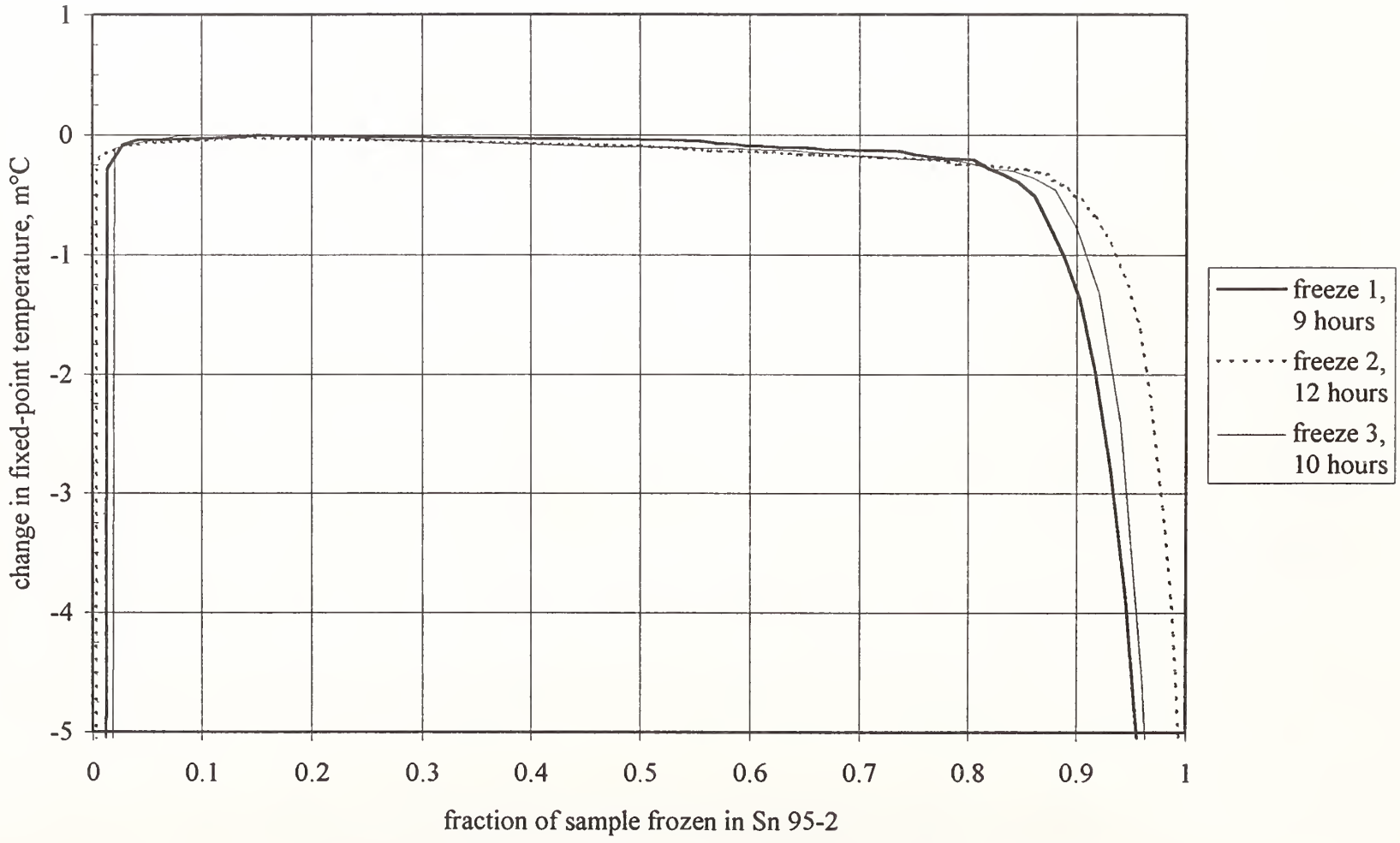

Figure 3. Three freezing curves for the SRM 1747 fixed-point cell Sn 95-2 using the "induced inner freeze" preparation technique.

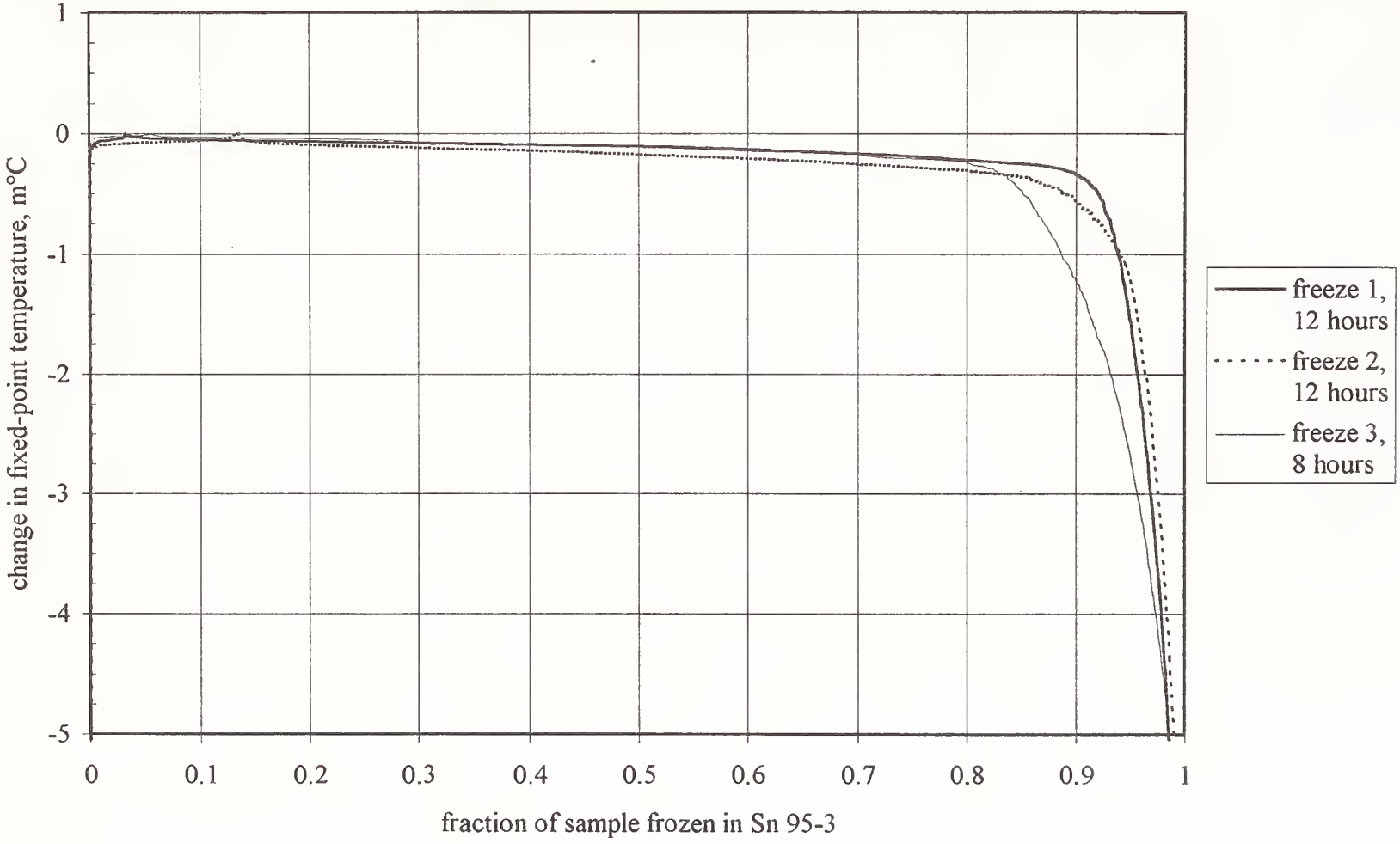

Figure 4. Three freezing curves for the SRM 1747 fixed-point cell Sn 95-3 using the "induced inner freeze" preparation technique.

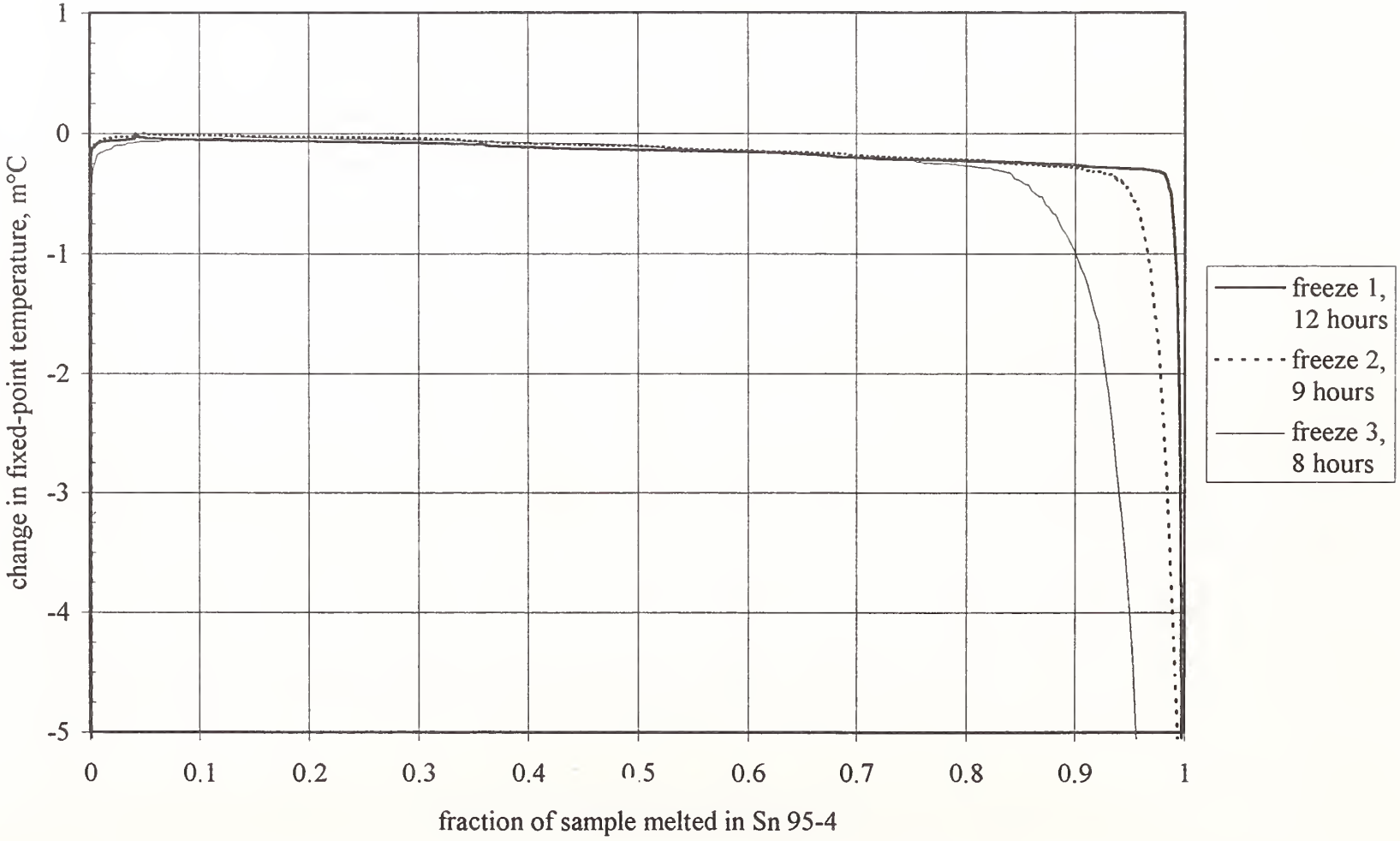

Figure 5. Three freezing curves for the SRM 1747 fixed-point cell Sn 95-4 using the "induced inner freeze" preparation technique.

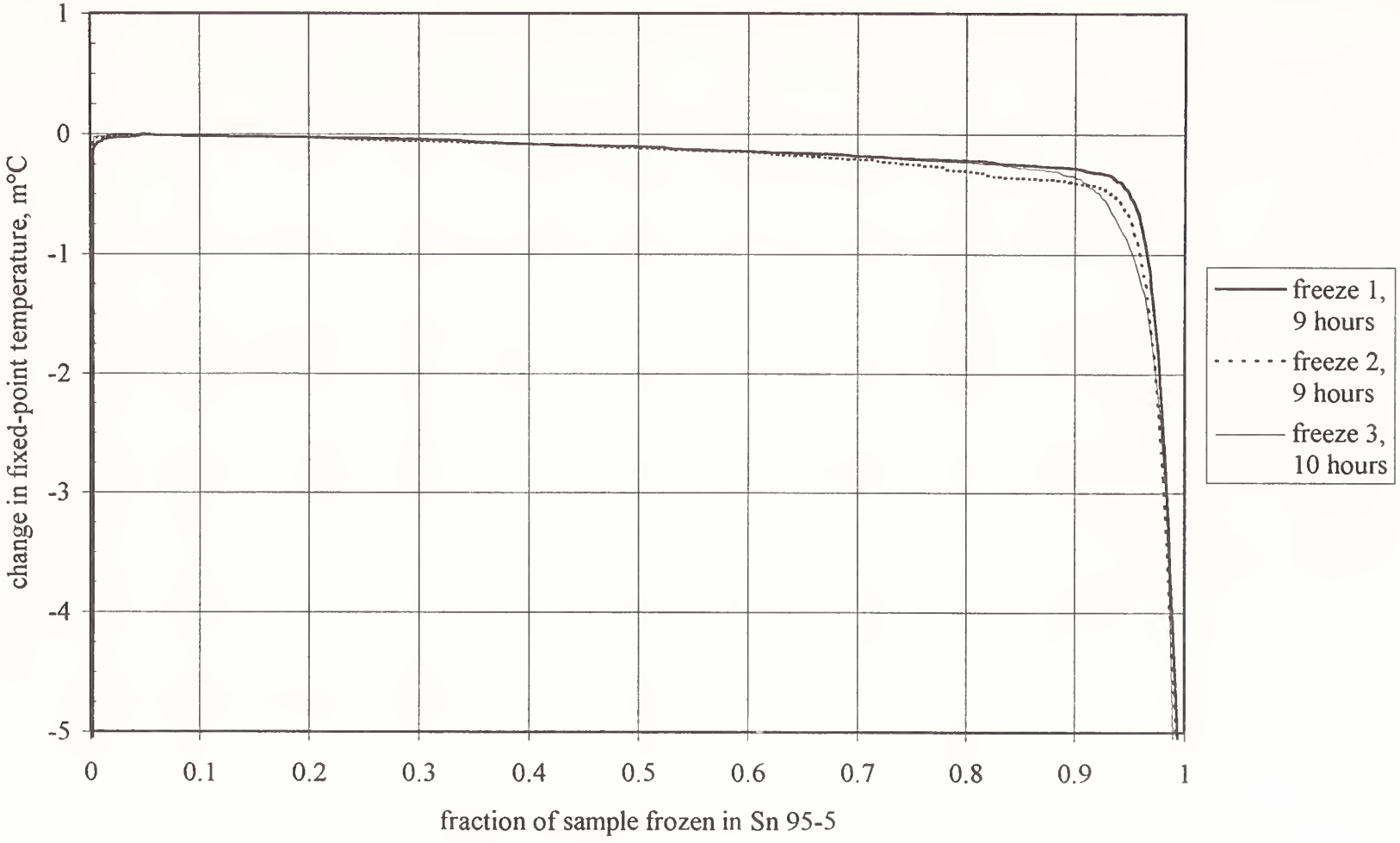

Figure 6. Three freezing curves for the SRM 1747 fixed-point cell Sn 95-5 using the "induced inner freeze" preparation technique.

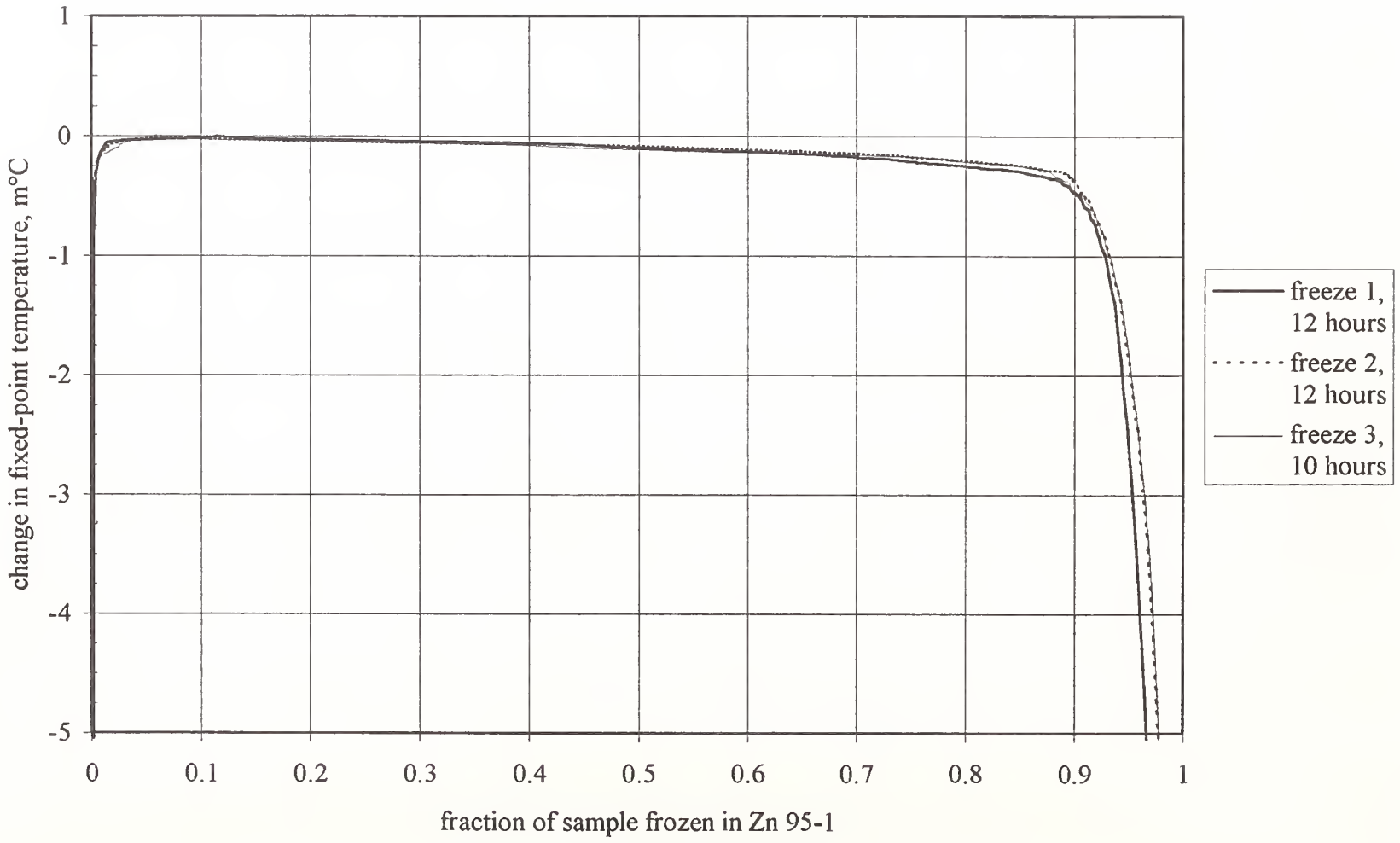

Figure 7. Three freezing curves for the SRM 1748 fixed-point cell Zn 95-1 using the "induced inner freeze" preparation technique.

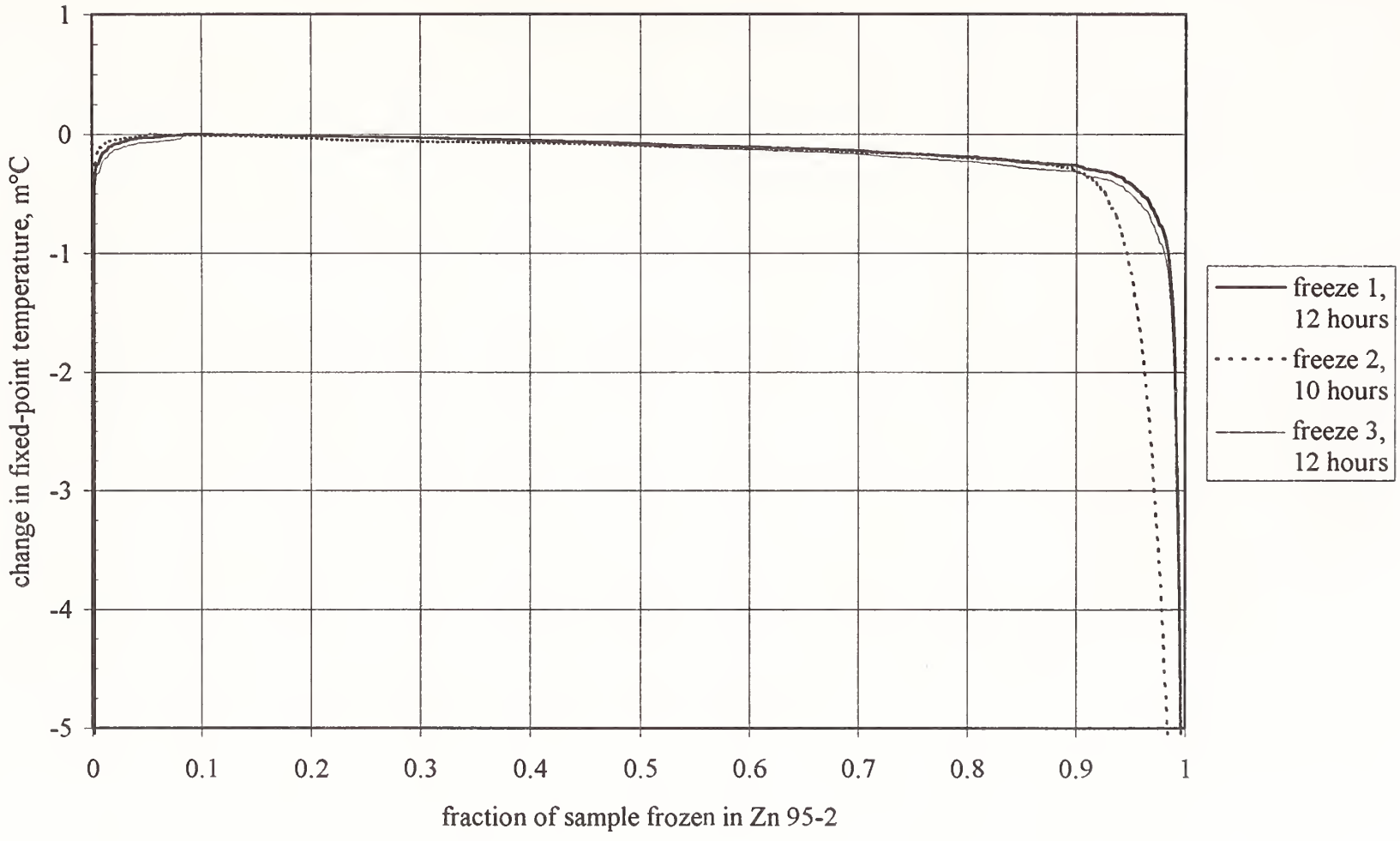

Figure 8. Three freezing curves for the SRM 1748 fixed-point cell Zn 95-2 using the "induced inner freeze" preparation technique.

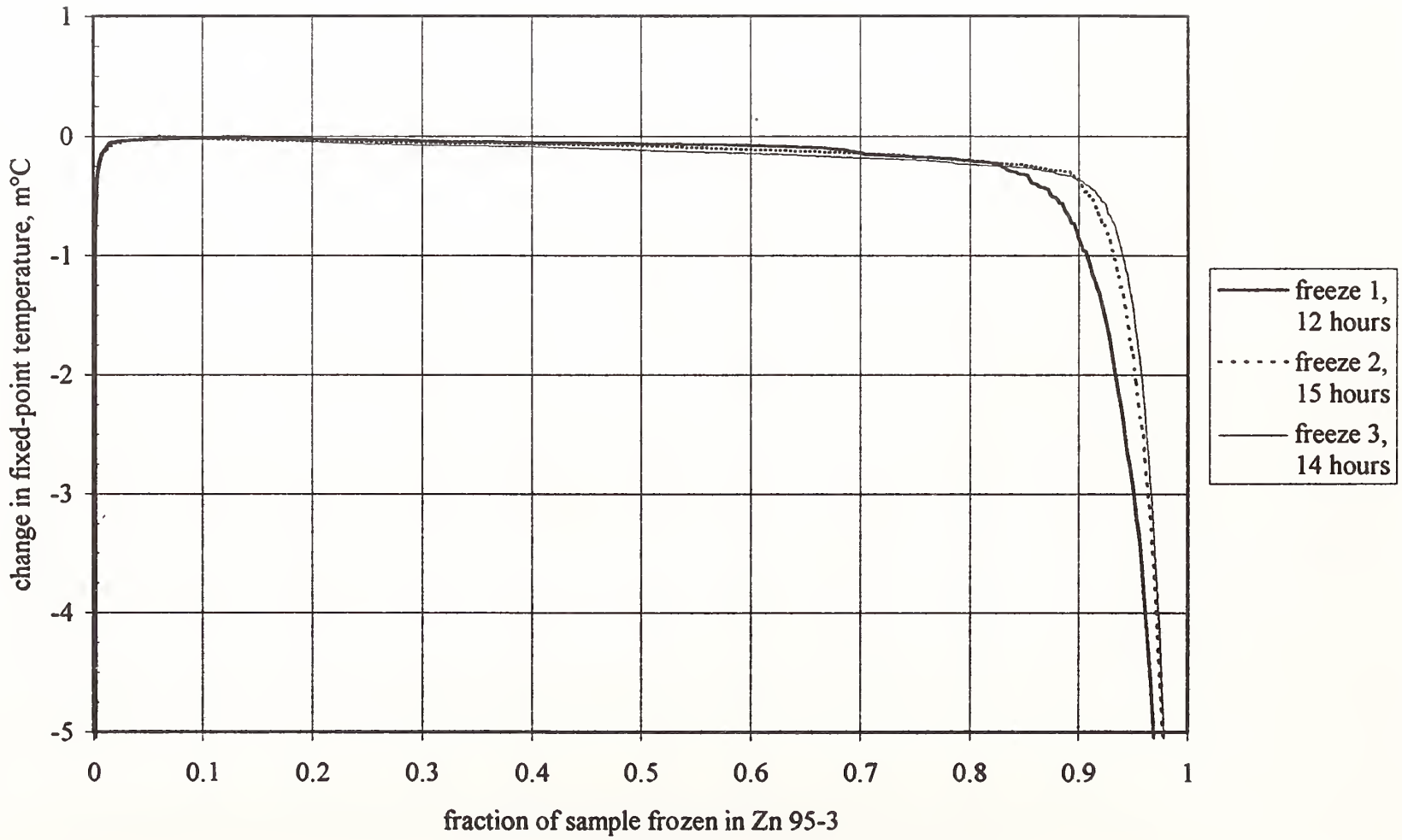

Figure 9. Three freezing curves for the SRM 1748 fixed-point cell Zn 95-3 using the "induced inner freeze" preparation technique.

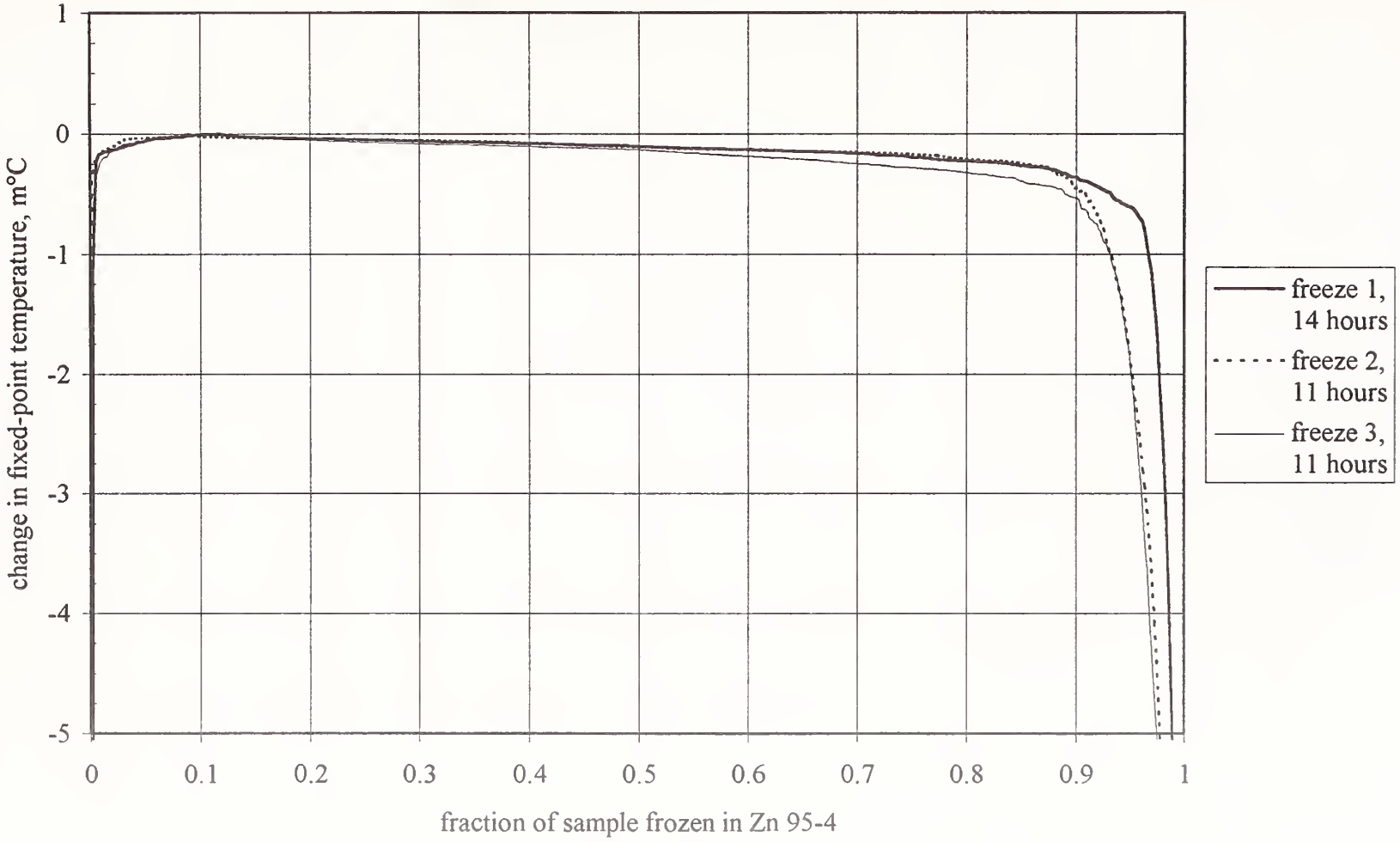

Figure 10. Three freezing curves for the SRM 1748 fixed-point cell Zn 95-4 using the "induced inner freeze" preparation technique.

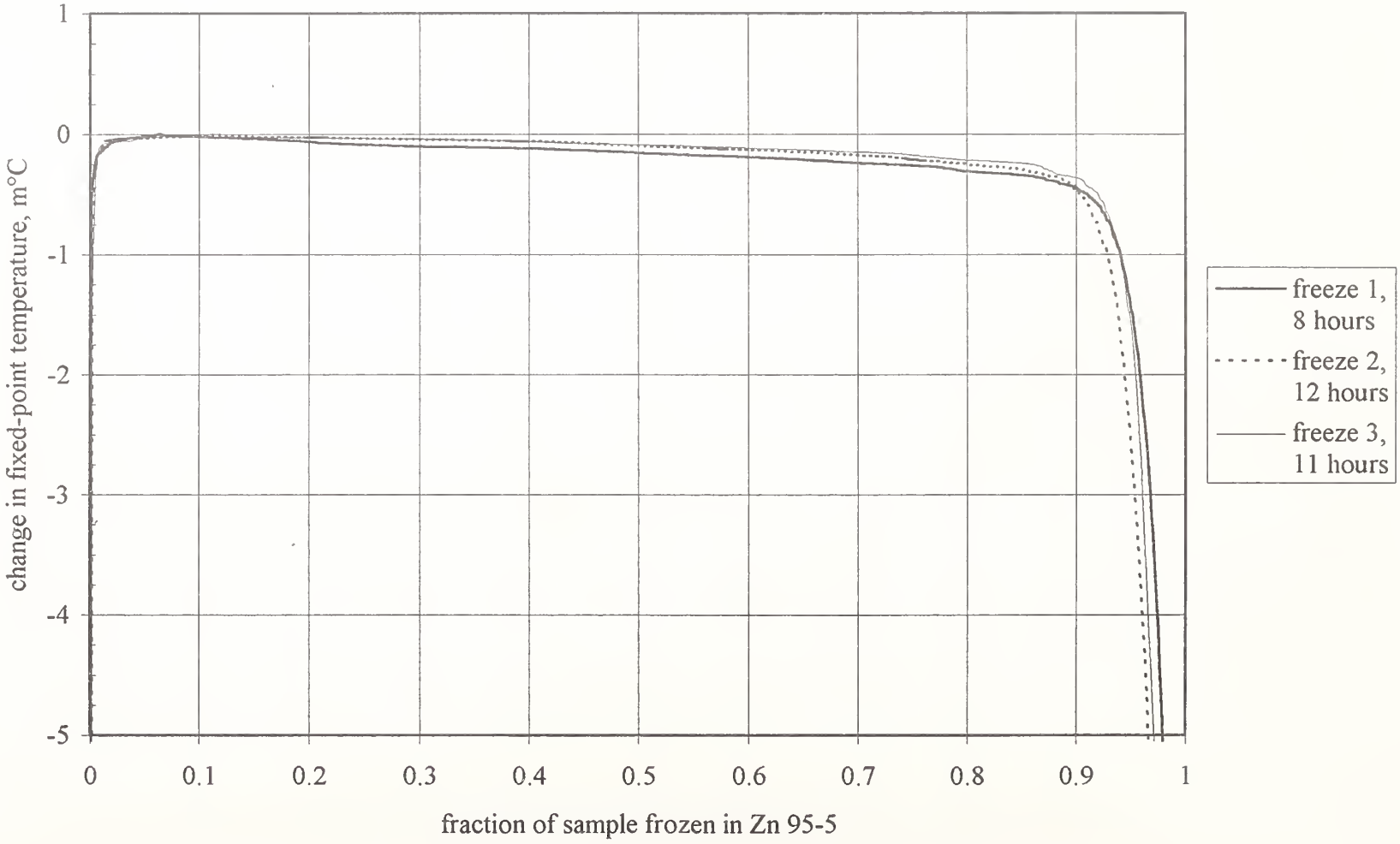

Figure 11. Three freezing curves for the SRM 1748 fixed-point cell Zn 95-5 using the "induced inner freeze" preparation technique.

frozen metal of the flat section of the plateaus was 0.0_8 m°C, 0.0_9 m°C, 0.1_3 m°C, 0.1_1 m°C and 0.1_1 m°C for Sn 95-1, Sn 95-2, Sn 95-3, Sn 95-4 and Sn 95-5, respectively. For the Zn freezing curve plateaus in figures 7 to 11, the average estimated temperature depression from the extrapolated 0% frozen metal (time of recalescence) to the 50% frozen metal of the flat section of the plateaus was 0.1_0 m°C, 0.0_9 m°C, 0.0_9 m°C, 0.1_2 m°C and 0.1_2 m°C for Zn 95-1, Zn 95-2, Zn 95-3, Zn 95-4 and Zn 95-5, respectively.

For both the Sn and Zn freezing-point cells, the experimentally determined temperature depressions are smaller than the calculated value. Differences between the calculated and the experimentally derived temperature depression may indicate either an uncertainty in using Raoult's Law of dilute solutions, an uncertainty in the extrapolation method chosen to derive the temperature depression or an uncertainty in the impurities specified in the emission spectrographic assay.

4.2 Analysis of SRM melting-point curves

Figures 12 to 16 show the melting curves for each of the five Sn fixed-point cells. Using an excitation current of 1 mA, thermometer readings were recorded continuously until the melting was complete. The average length of a melt for both the five Sn cells and five Zn cells was 8 hours. The time-temperature relationship shown in the figures are calculated from the change in resistance of the SPRT during a melting-point realization. For comparison purposes, the three melting curves for each cell shown the figures were normalized so that SPRT resistance equivalent to 50% melted sample passes through the 0 m°C point on the graph. From the graphs, the average temperature range of the melting curves were 0.4 m°C, 0.5 m°C, 0.5 m°C, 0.4 m°C and 0.4 m°C for Sn 95-1, Sn 95-2, Sn 95-3, Sn 95-4 and Sn 95-5, respectively. Figures 17 to 21 show the melting curves for each of the five Zn fixed-point cells. From the graphs, the average temperature range of the melting curves were 0.4 m°C, 0.4 m°C, 0.6 m°C, 0.5 m°C and 0.6 m°C for Zn 95-1, Zn 95-2, Zn 95-3, Zn 95-4 and Zn 95-5, respectively.

While the temperature range of a melting curve is not indicative of the purity of the metal, an analysis of the difference in the liquidus-point temperatures obtained from a slow freeze ($\geq$10 hours) and from a melt after a fast freeze may be performed. A good cell will have a difference that is less than 0.2 m°C [9]. The differences in the liquidus-point temperatures for the Sn cells were about 0.1 m°C and about 0.2 m°C for the Zn cells.

4.3 Analysis of SRM direct comparisons

The second part of the certification was a direct comparison of the fixed-point cells under test with the laboratory standard fixed-point cell (Sn 88A or Zn 93-4) to determine their freezing-point temperatures relative to that of the reference cell. Figure 22 shows the results of the direct comparison of the five SRM Sn cells with the laboratory standard. The set of matching symbols (open and closed) are for the direct comparison measurements of Sn 95-X (where X is 1, 2, 3, 4 or 5) compared with Sn 88A. The average temperature difference of the first readings of each direct comparison showed that Sn 95-1, Sn 95-2, Sn 95-3, Sn 95-4 and Sn 95-5 were 0.0_5 m°C, 0.0_9 m°C,

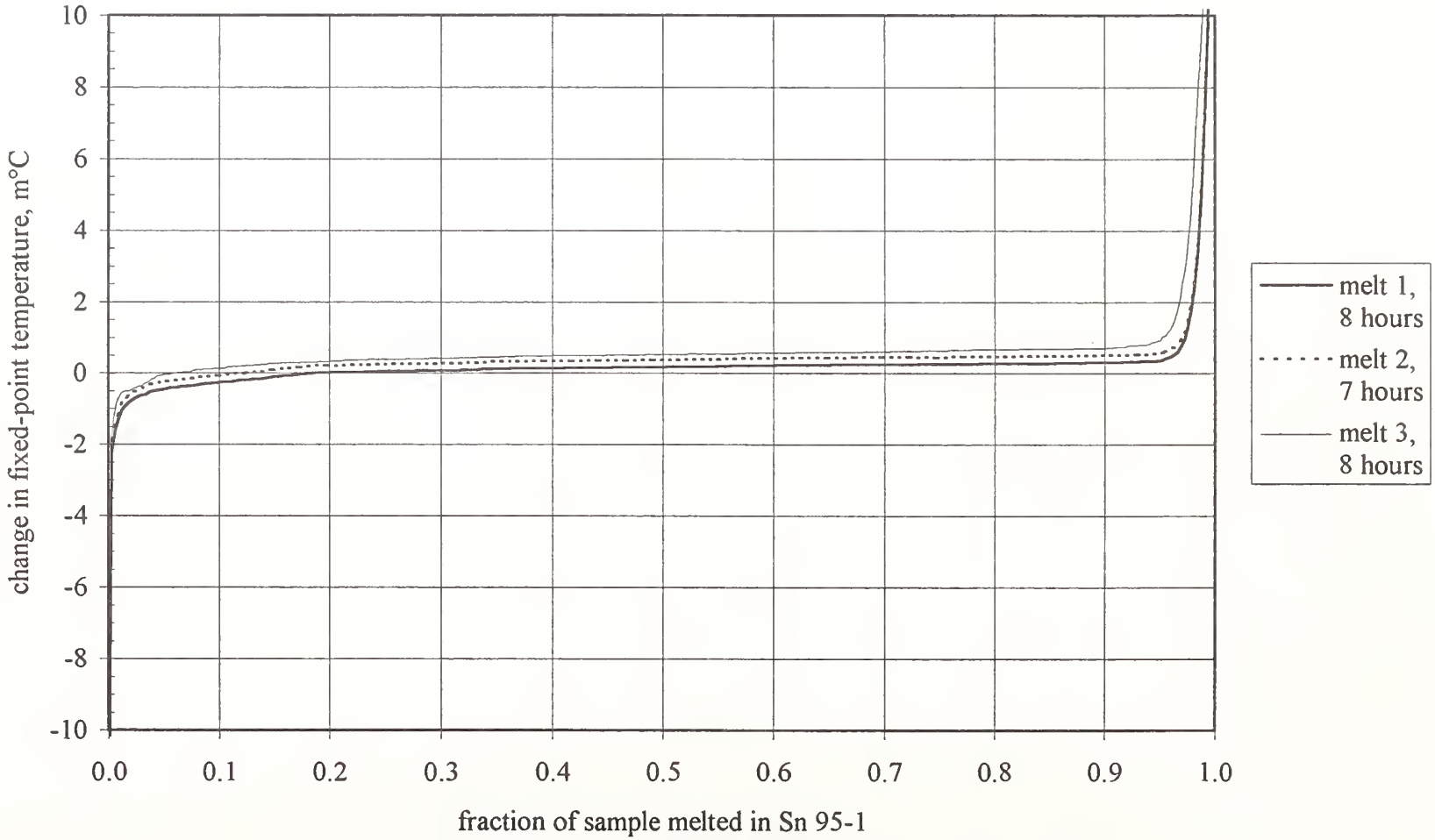

Figure 12. Three melting curves for the SRM 1747 fixed-point cell Sn 95-1 following a slow freeze. Each melt followed the respective slow freeze of Figure 2.

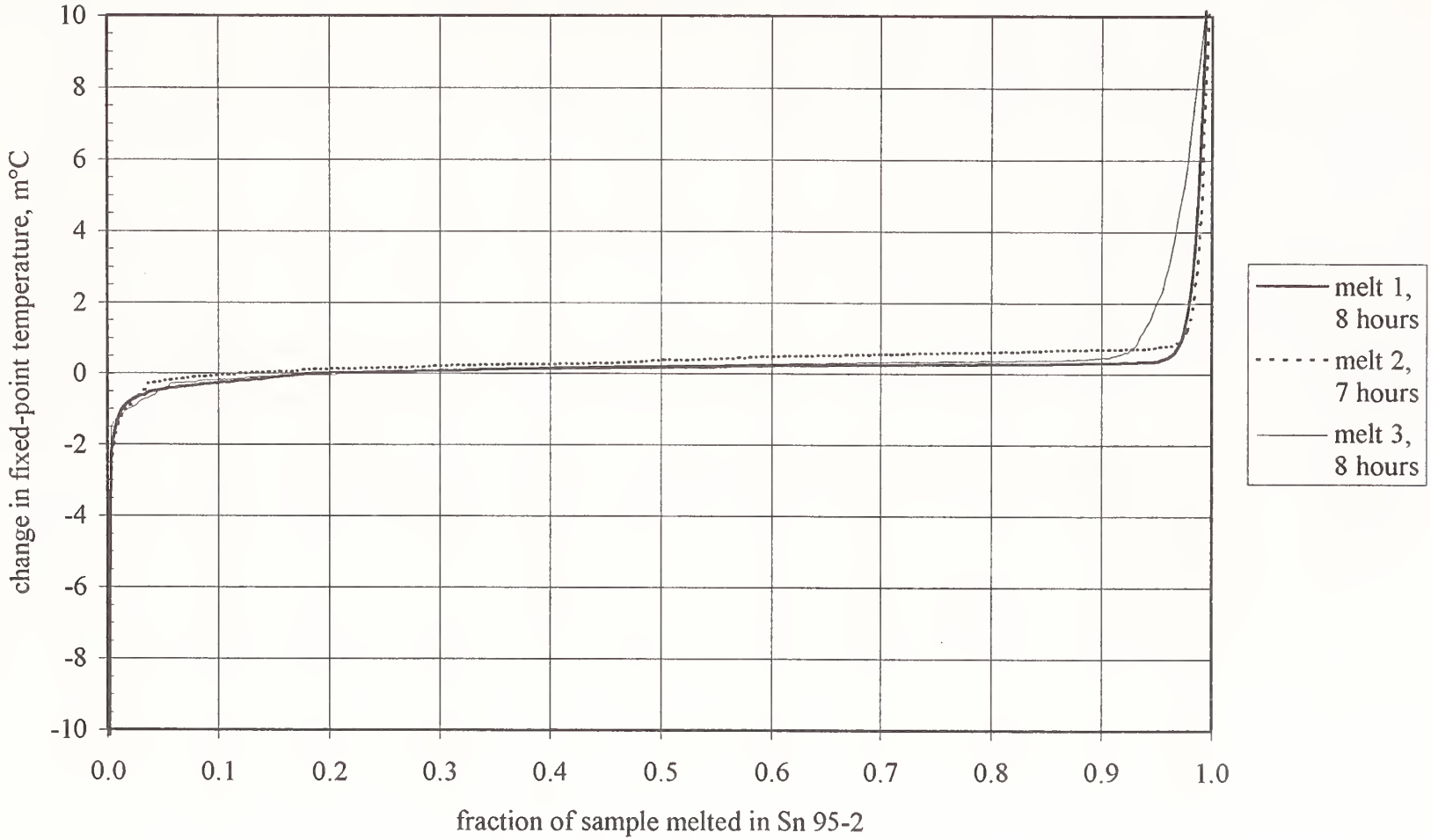

Figure 13. Three melting curves for the SRM 1747 fixed-point cell Sn 95-2 following a slow freeze. Each melt followed the respective slow freeze of Figure 3.

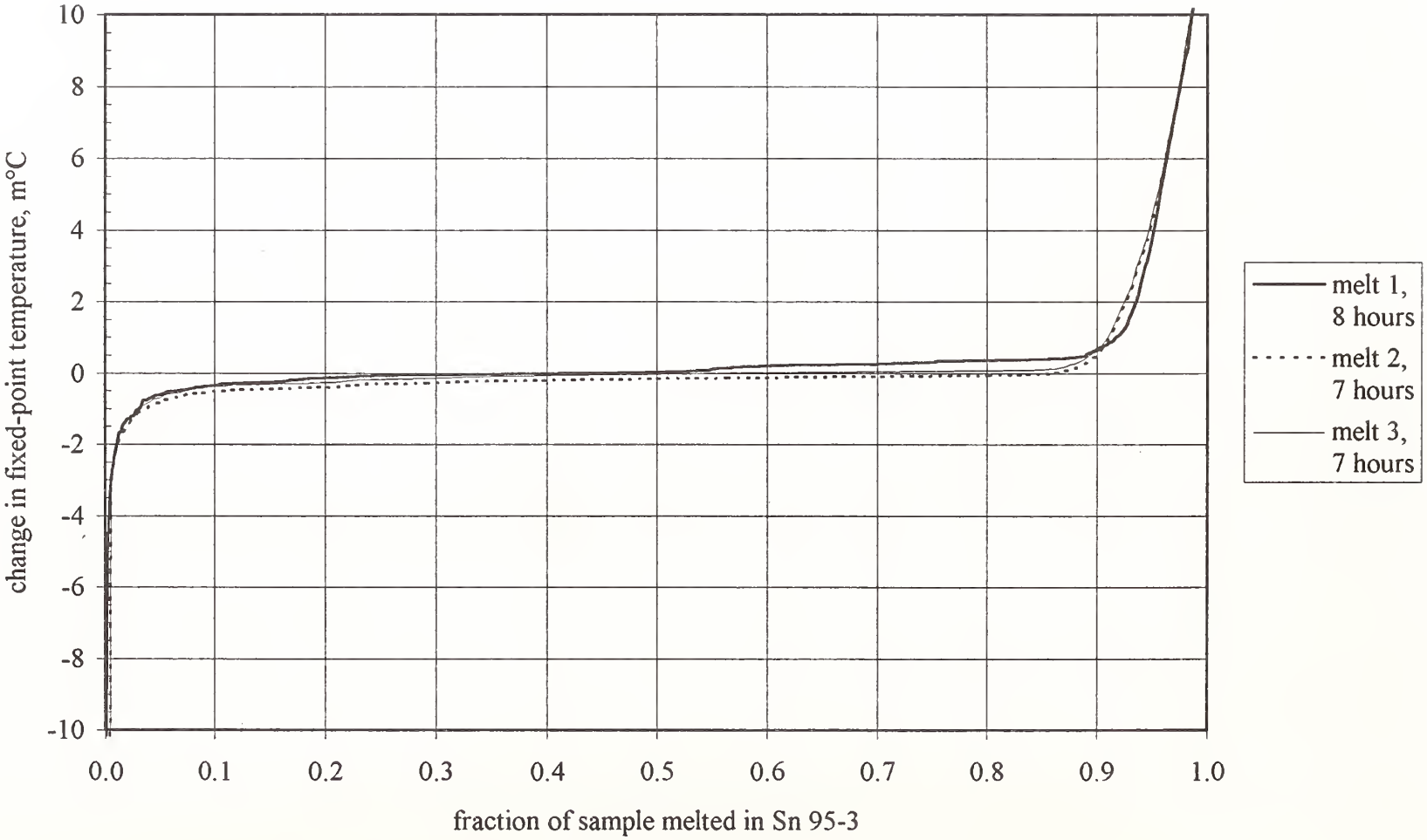

Figure 14. Three melting curves for the SRM 1747 fixed-point cell Sn 95-3 following a slow freeze. Each melt followed the respective slow freeze of Figure 4.

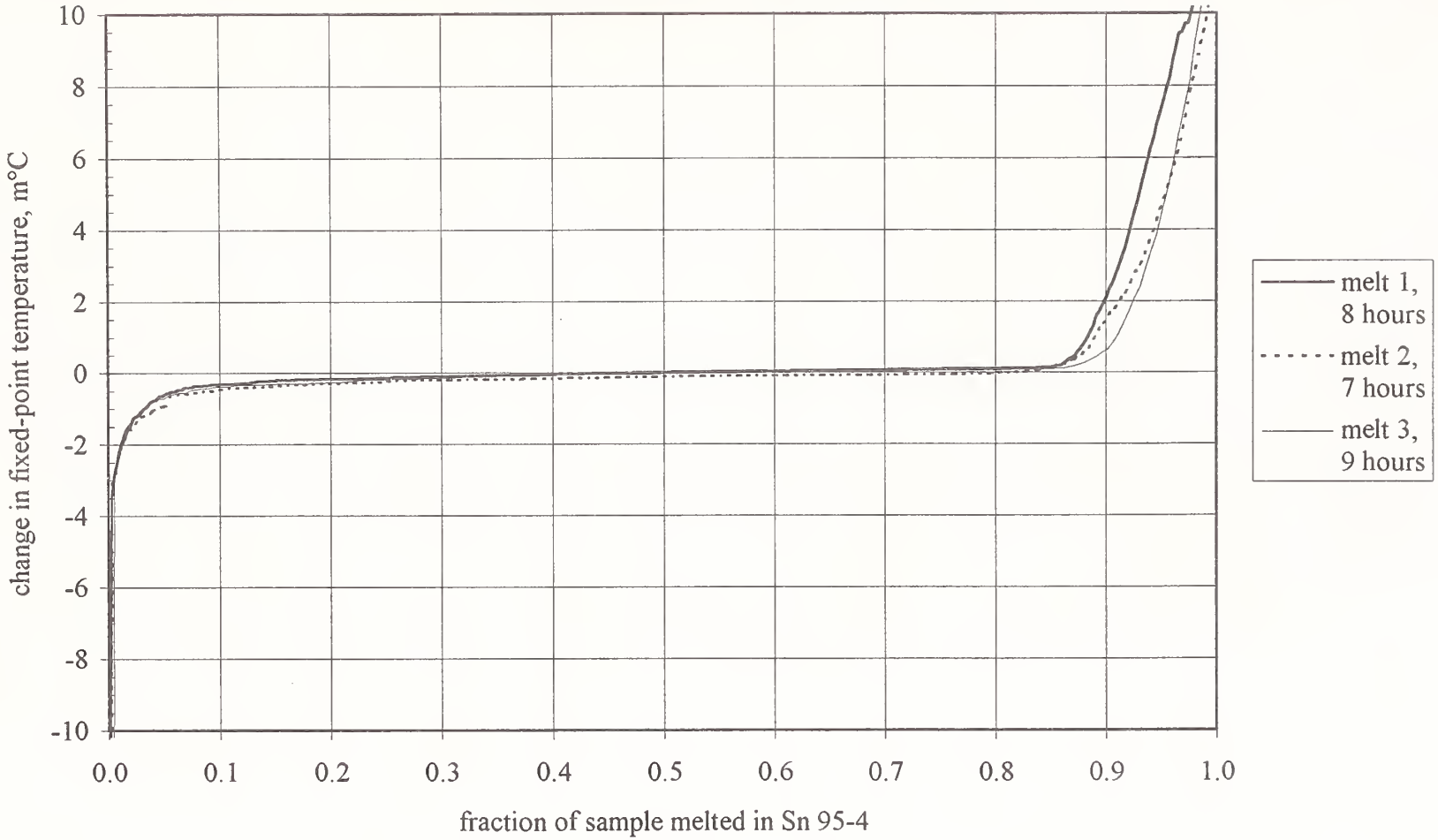

Figure 15. Three melting curves for the SRM 1747 fixed-point cell Sn 95-4 following a slow freeze. Each melt followed the respective slow freeze of Figure 5.

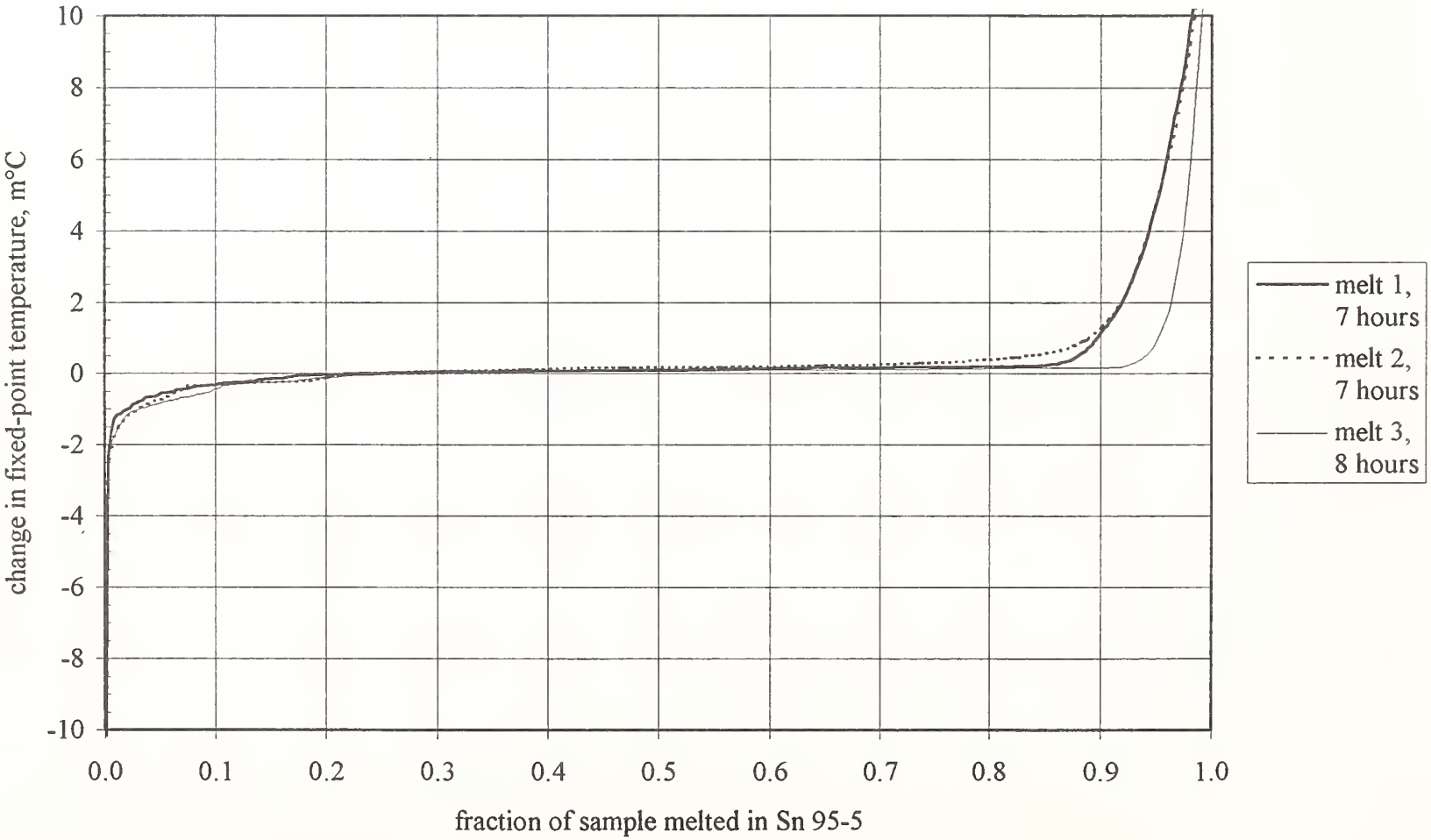

Figure 16. Three melting curves for the SRM 1747 fixed-point cell Sn 95-5 following a slow freeze. Each melt followed the respective slow freeze of Figure 6.

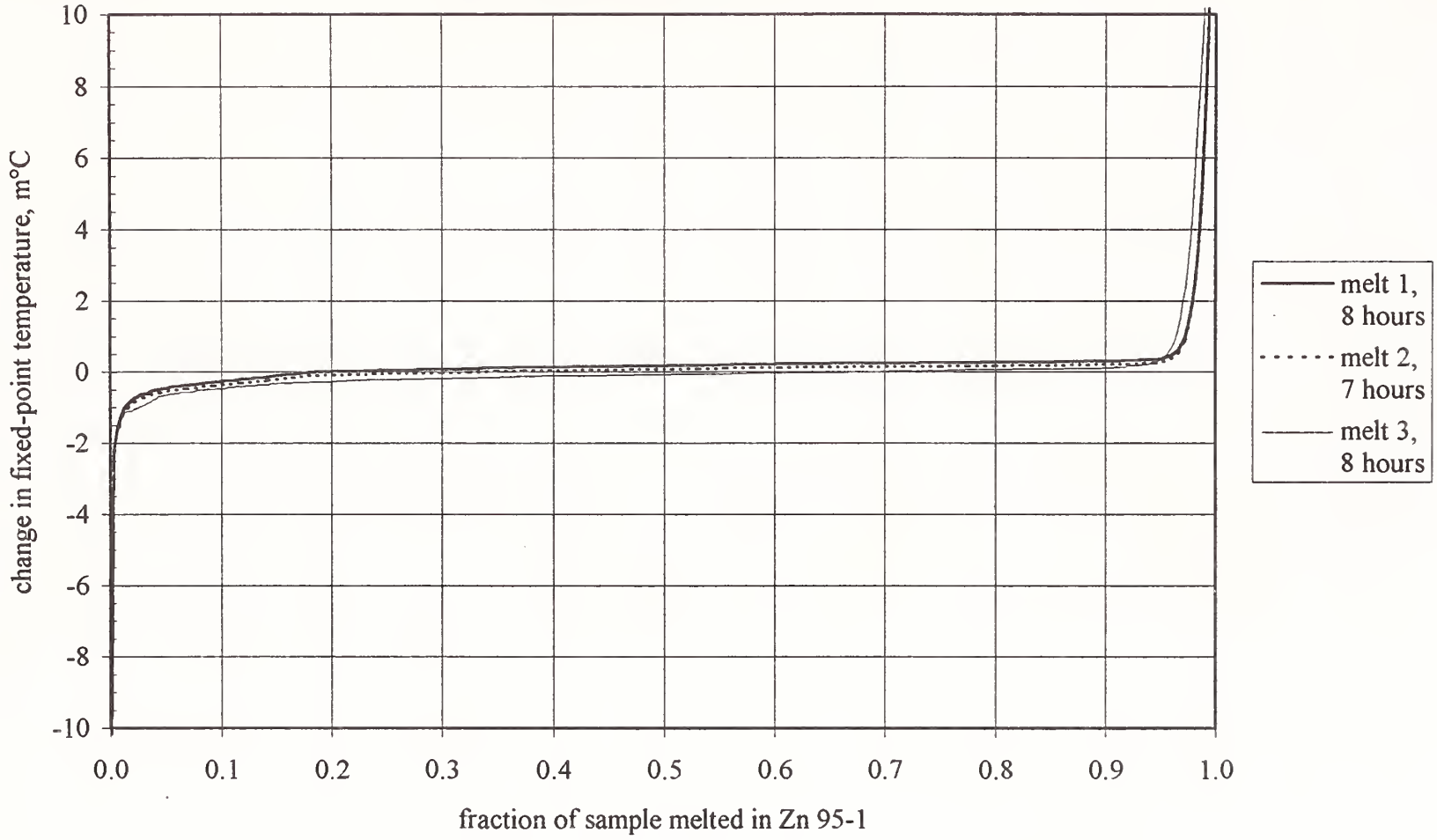

Figure 17. Three melting curves for the SRM 1748 fixed-point cell Zn 95-1 following a slow freeze. Each melt followed the respective slow freeze of Figure 7.

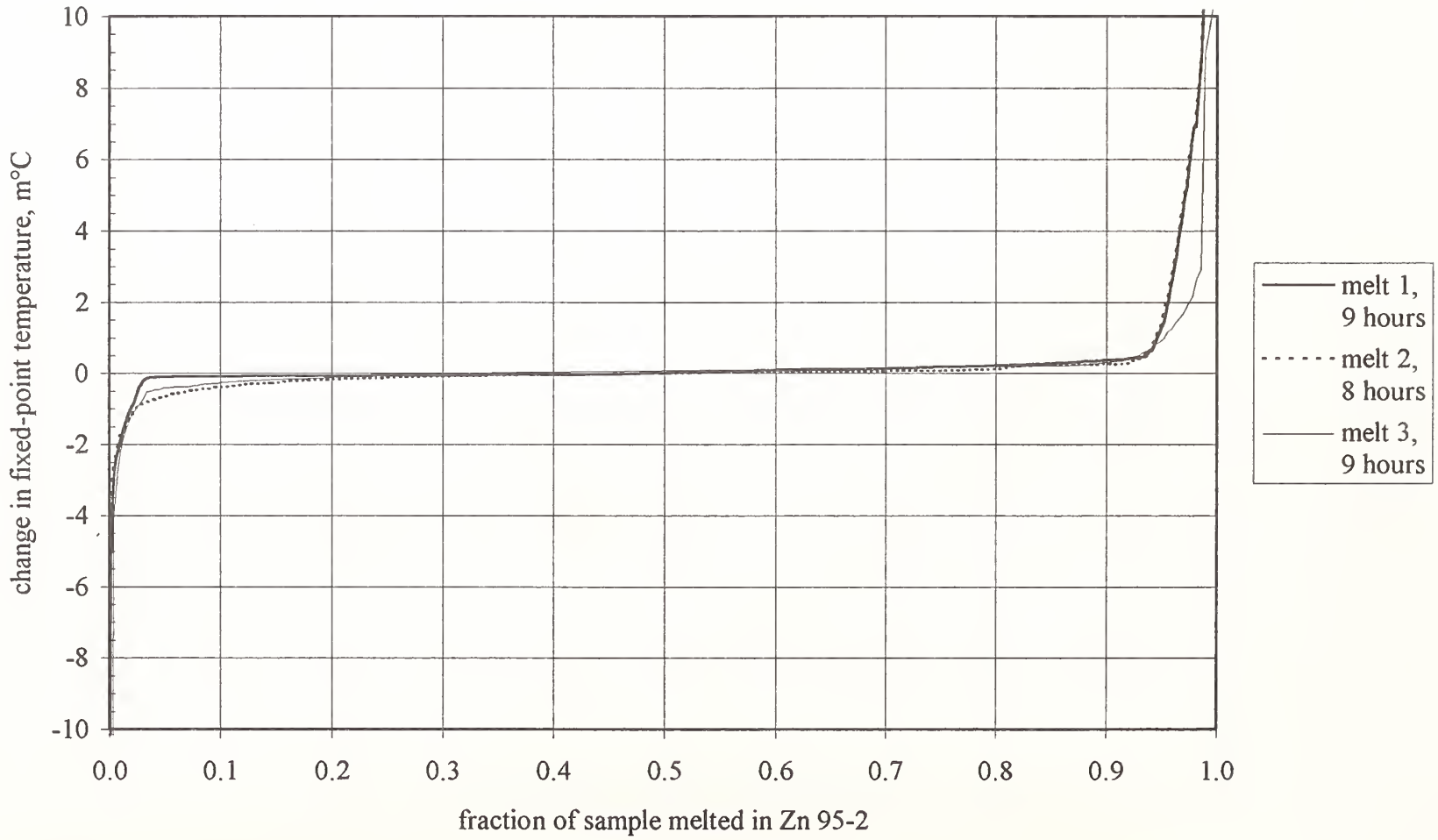

Figure 18. Three melting curves for the SRM 1748 fixed-point cell Zn 95-2 following a slow freeze. Each melt followed the respective slow freeze of Figure 8.

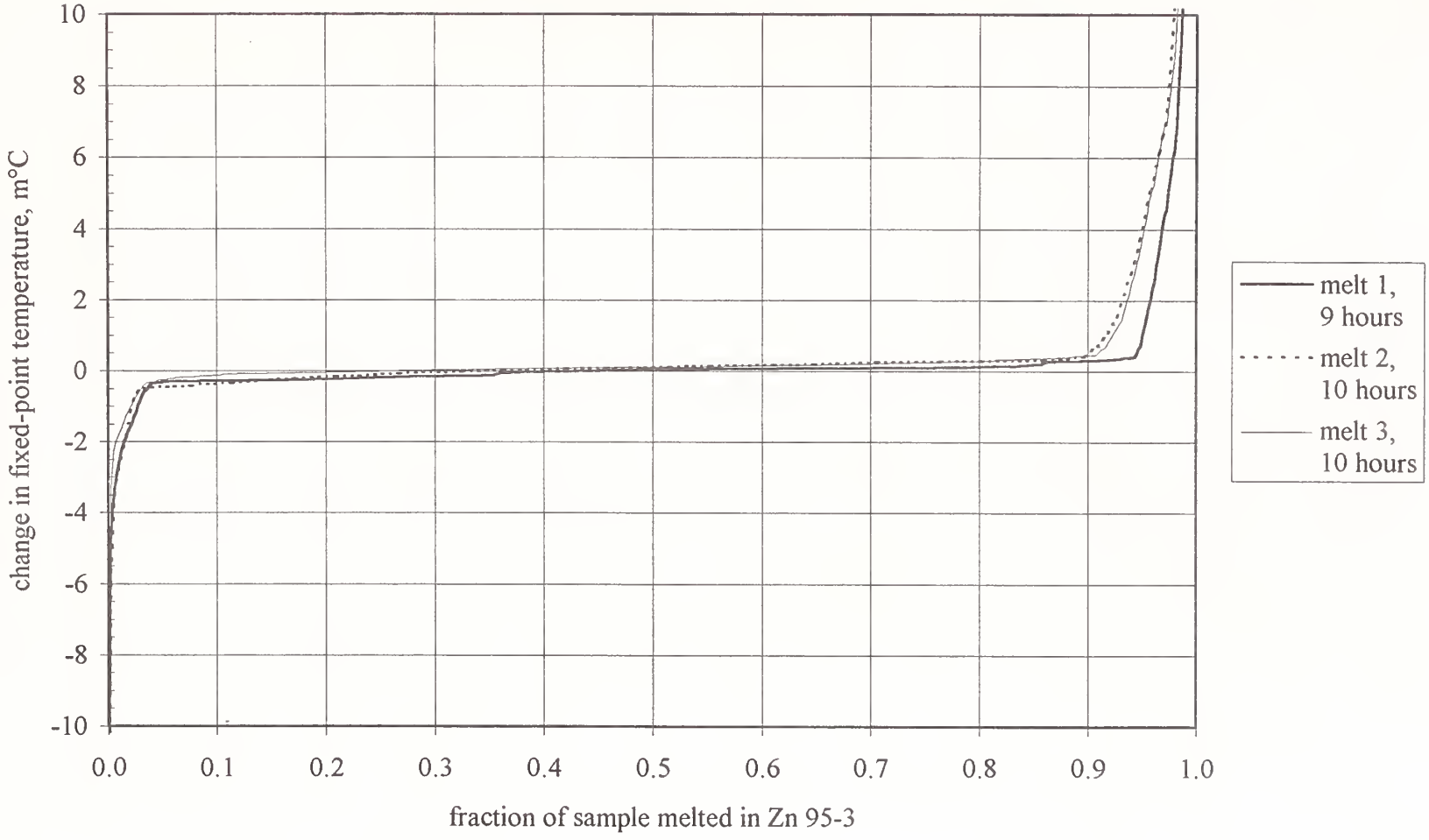

Figure 19. Three melting curves for the SRM 1748 fixed-point cell Zn 95-3 following a slow freeze. Each melt followed the respective slow freeze of Figure 9.

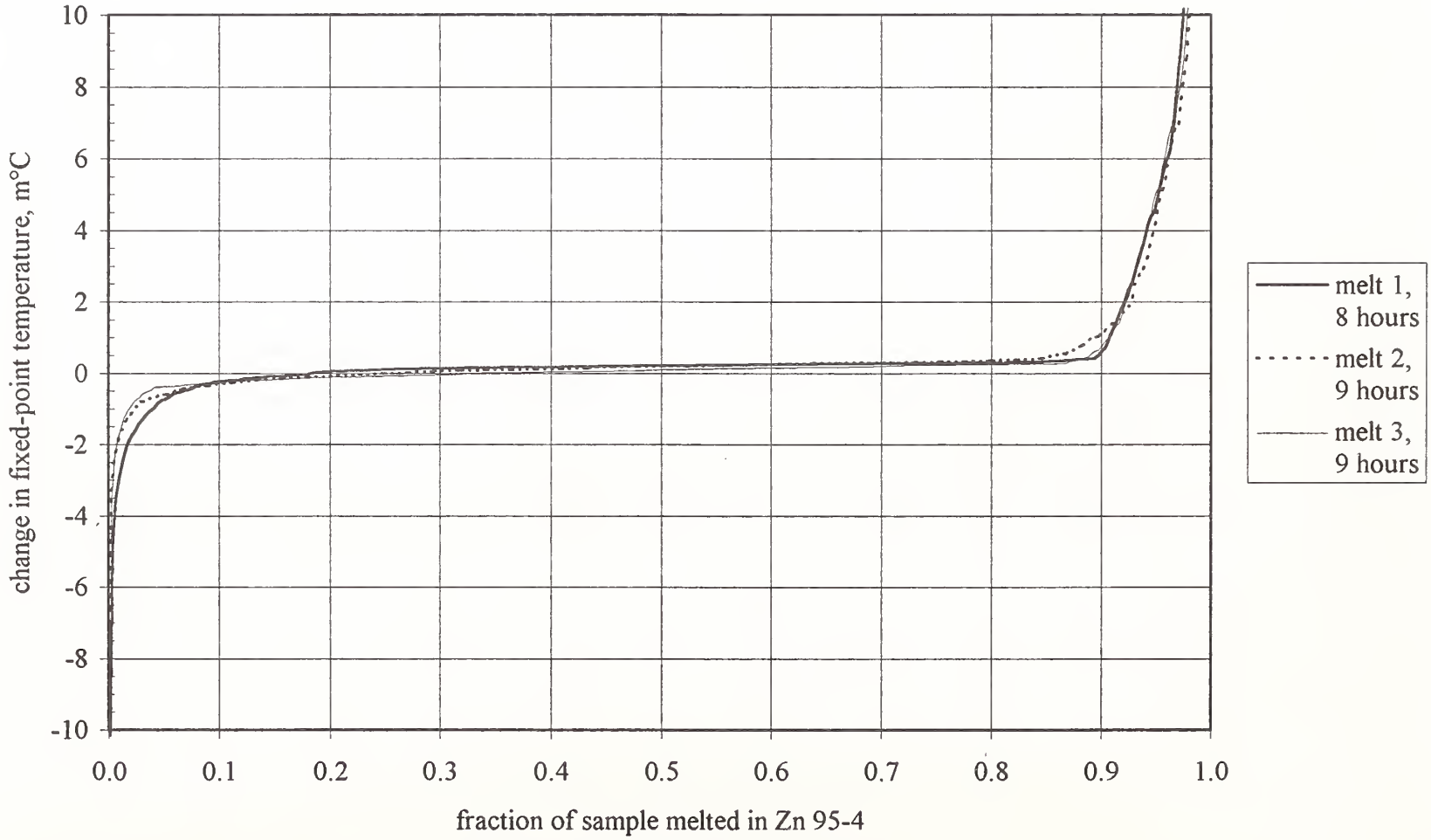

Figure 20. Three melting curves for the SRM 1747 fixed-point cell Zn 95-4 following a slow freeze. Each melt followed the respective slow freeze of Figure 10.

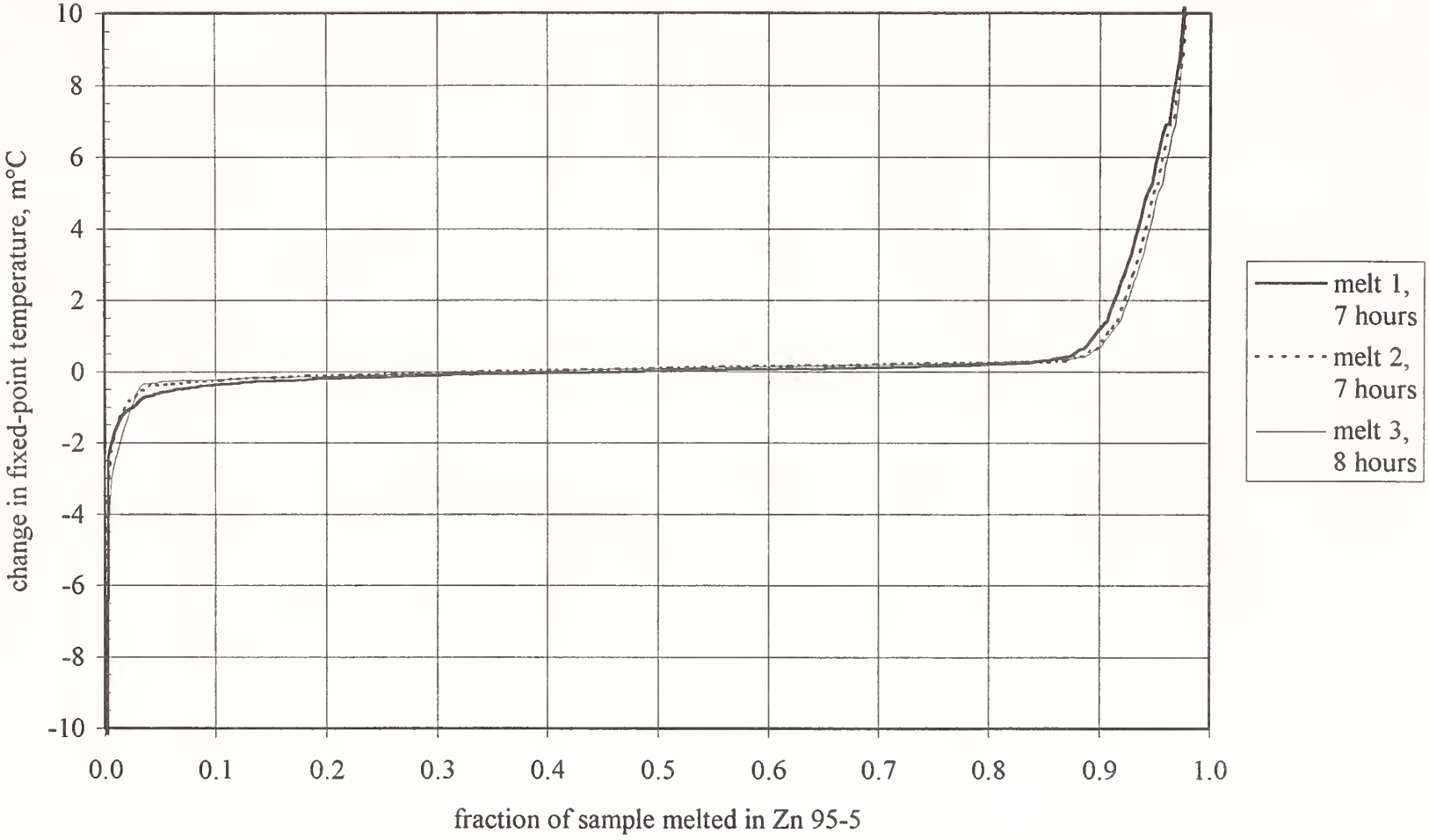

Figure 21. Three melting curves for the SRM 1748 fixed-point cell Zn 95-5 following a slow freeze. Each melt followed the respective slow freeze of Figure 11.

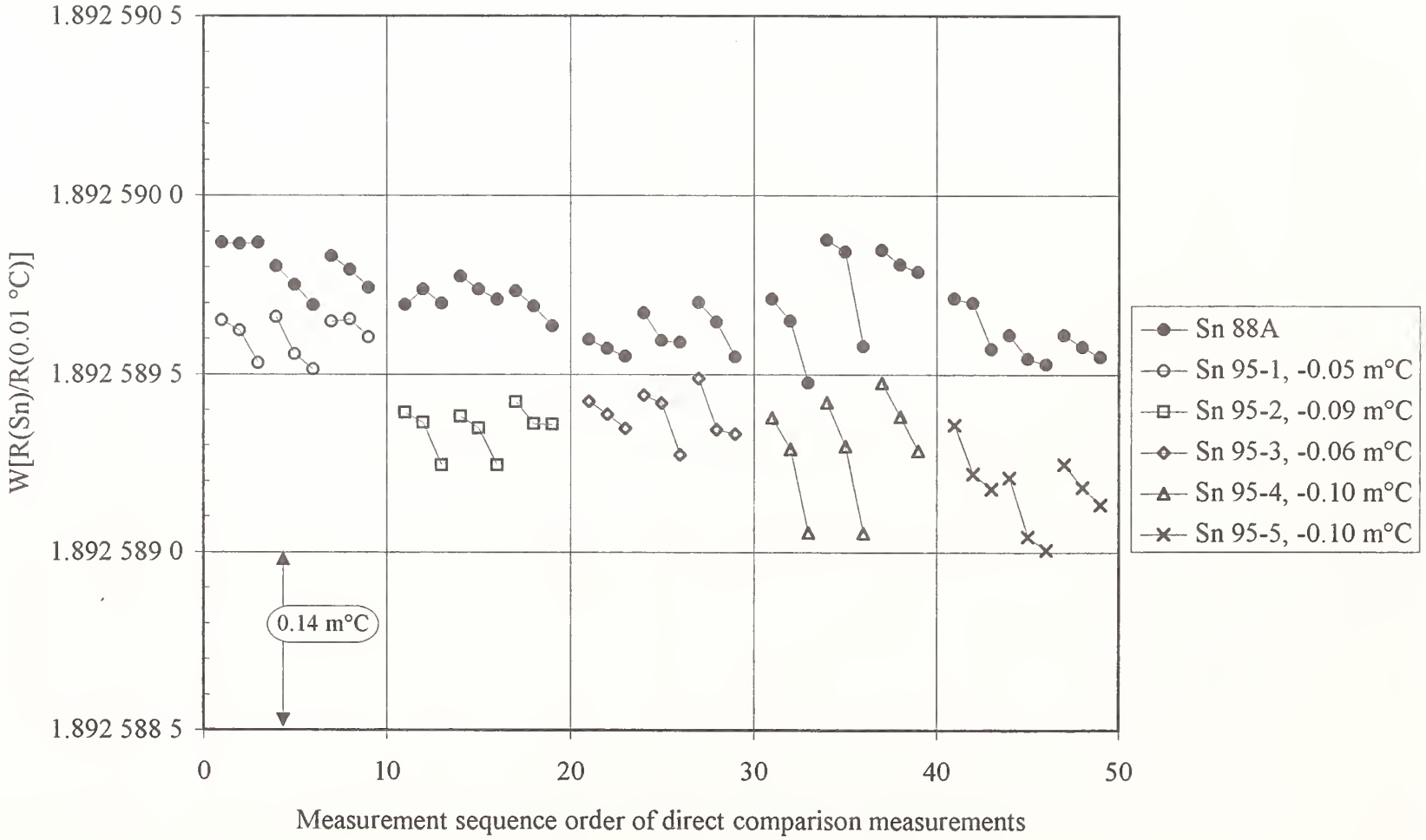

Figure 22. Direct freezing plateau comparison results of SRM 1748 freezing-point cells Sn 95-1, Sn 95-2, Sn 95-3, Sn 95-4 and Sn 95-5 with Sn 88A (laboratory standard). The differences shown in the legend represent the average temperature difference from the first readings of each direct comparison. Each set of symbols connected by lines are for the direct comparison measurements made during the simultaneous freezes.

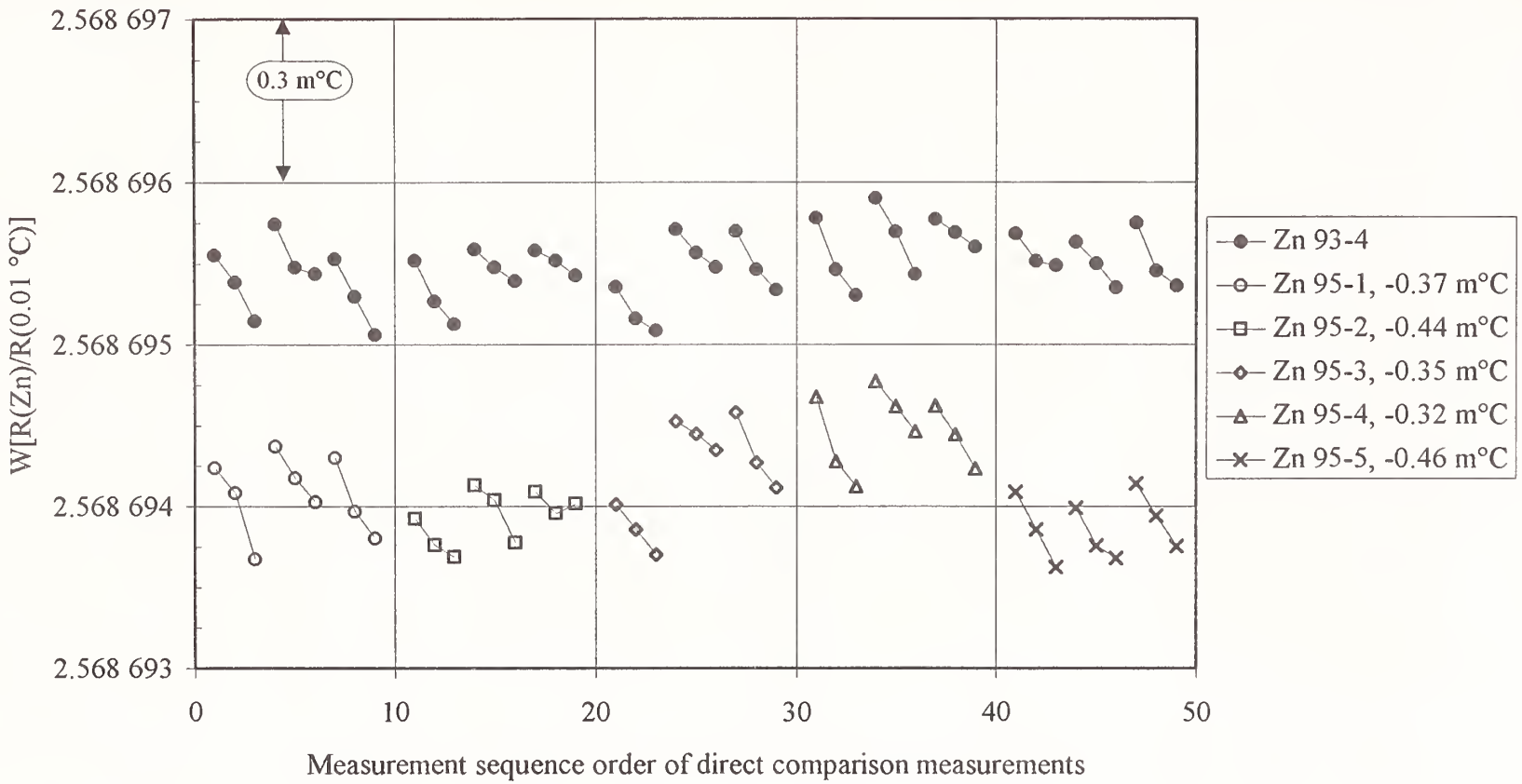

Figure 23. Direct freezing plateau comparison results of SRM 1748 freezing-point cells Zn 95-1, Zn 95-2, Zn 95-3, Zn 95-4 and Zn 95-5 with Zn 93-4 (laboratory standard). The differences shown in the legend represent the average temperature difference from the first readings of each direct comparison. Each set of symbols connected by lines are for the direct comparison measurements made during the simultaneous freezes.

0.0_6 m°C, 0.1_0 m°C and 0.1_0 m°C colder than the laboratory standard. Figure 23 shows the results of the direct comparison of the five SRM Zn cells with the laboratory standard. The set of matching symbols (open and closed) are for the direct comparison measurements of Zn 95-X (where X is 1, 2, 3, 4 or 5) compared with Zn 93-4. The average temperature difference of the first readings of each direct comparison showed that Zn 95-1, Zn 95-2, Zn 95-3, Zn 95-4 and Zn 95-5 were 0.3_7 m°C, 0.4_4 m°C, 0.3_5 m°C, 0.3_2 m°C and 0.4_6 m°C colder than the laboratory standard. Each set of symbols (open or closed) connected by lines are for the direct comparison measurements made during the simultaneous freezes.

5. Uncertainties

The expanded uncertainty U assigned to the measurements was calculated from the equation:

$$U = k\sqrt{s^2 + \sum u(i)^2} \qquad (1)$$

where k is the coverage factor, s is the Type A standard uncertainty calculated from the standard deviation of the mean of the W [$W=R(t_{90})/R(0.01\ °C)$] values obtained from the direct comparison measurements and $u(i)$ is the estimated Type B standard uncertainty for each known component in the measurement process that cannot be directly measured [10,11].

5.1 Uncertainty of direct comparison measurements

Many of the systematic effects in measurement process cancel because the measurements being analyzed are from the direct comparisons of fixed-point cells. There were two known contributions to the Type A standard uncertainty; one from the instrumental measurements themselves and the second from the handling of the SPRT during transfer from cell to cell.

The value of the Type A standard uncertainty for the measurements was at most 0.01_0 m°C for SRM 1747 and at most 0.01_8 m°C for SRM 1748. The two contributions attributed to the Type A standard uncertainty were at most 0.00_8 m°C and 0.00_6 m°C from the instrumentation and at most 0.00_8 m°C and 0.01_7 m°C from handling of the SPRT for SRMs 1747 and 1748, respectively.

There were three known contributions to the Type B standard uncertainty in the direct comparison measurements. These were the uncertainty in the exact immersion depth of the SPRT due to the uncertainty in the position of the thermometer sensor during measurements, the uncertainty in the immersion depth of the thermometer due to the uncertainty in the exact fraction of the metal sample frozen, and the uncertainty in the adequacy of immersion of the thermometer to eliminate the thermometer stem conduction during the intercomparisons.

The Type B standard uncertainty from the three known contributions in the direct comparison measurements for both cells (SRM cell and the reference cell) was 0.00_9 m°C for SRM 1747 and 0.01_3 m°C for SRM 1748. The uncertainty in the exact immersion depth of the SPRT due to the

uncertainty in the position of the thermometer sensor during measurements gives an uncertainty of 1.3 μ°C for SRM 1747 and 1.6 μ°C for SRM 1748. The uncertainty in the immersion depth of the thermometer due to the uncertainty in the exact fraction of the metal sample frozen gives an uncertainty of 0.2 μ°C for SRM 1747 and 0.6 μ°C for SRM 1748. The uncertainty in the adequacy of immersion of the thermometer to eliminate the thermometer stem conduction during the intercomparisons gives an uncertainty of 6.5 μ°C for SRM 1747 and 9.2 μ°C for SRM 1748.

The expanded uncertainty (k=2) in the intercomparison measurements of SRM 1747 is 0.02_7 m°C and 0.04_4 m°C for SRM 1748.

5.2 Uncertainty assigned to SRM fixed-point cells

The expanded uncertainty (k=2) [10,11] assigned to each of the SRM 1747 Sn freezing-point cells is given in Table 1. The Type A standard uncertainty of 0.15 m°C is the standard deviation of $W(t_{90})$ values of repeated measurements of the laboratory standard cell with a check SPRT [12]. The Type B standard uncertainty is obtained from the estimated uncertainty of 0.09 m°C in the freezing-point temperature of the laboratory standard calculated from the impurities listed in the metal assay [12], the temperature difference between the SRM cell and the laboratory standard cell as determined from the intercomparison measurements (see Section 4.3), and the uncertainty in those intercomparison measurements (see Section 5.1).

The expanded uncertainty (k=2) [10,11] assigned to each of the SRM 1748 Zn freezing-point cells is given in Table 2. The Type A standard uncertainty of 0.3 m°C is the standard deviation of $W(t_{90})$ values of repeated measurements of the laboratory standard cell with a check SPRT [12]. The Type B standard uncertainty is obtained from the estimated uncertainty of 0.17 m°C in the freezing-point temperature of the laboratory standard calculated from the impurities listed in the metal assay [12], the temperature difference between the SRM cell and the laboratory standard cell as determined from the intercomparison measurements (see Section 4.3), and the uncertainty in those intercomparison measurements (see Section 5.1).

Table 1. Estimate of uncertainties assigned to SRM 1747 Sn freezing-point cells.

SRM 1747 Freezing-Point Cell	Type A Standard Uncertainty m°C	Type B Standard Uncertainty m°C	Expanded Uncertainty, k=2 m°C
Sn 95-1	0.15	0.10	0.36
Sn 95-2	0.15	0.13	0.39
Sn 95-3	0.15	0.11	0.37
Sn 95-4	0.15	0.14	0.40
Sn 95-5	0.15	0.14	0.40

Table 2. Estimate of uncertainties assigned to SRM 1748 Zn freezing-point cells.

SRM 1748 Freezing-Point Cell	Type A Standard Uncertainty m°C	Type B Standard Uncertainty m°C	Expanded Uncertainty, k=2 m°C
Zn 95-1	0.3	0.41	1.0_1
Zn 95-2	0.3	0.47	1.1_2
Zn 95-3	0.3	0.39	0.9_8
Zn 95-4	0.3	0.36	0.9_4
Zn 95-5	0.3	0.49	1.1_4

6. Application

Prior to use of one of these SRM cells, the cell should be evacuated and backfilled with an inert gas (He or Ar) several times to remove any air present in the cell. During use, the cell should have a slight overpressure of an inert gas (He or Ar) of about 250 Pa above atmospheric to prevent air from entering the cell. To prevent possible breakage of the fixed-point cell and to ensure correct formation and advancement of the solid/liquid interfaces, the temperature gradient in the furnace used for realizing the fixed point should be small (≤ 10 m°C) over the crucible length (see Section 3.1).

In using one of these SRM cells, a long-stem SPRT should be associated with the fixed-point cell to act as a check thermometer for use during calibration. The check thermometer should be used to measure the beginning of each freeze prior to measurement of test thermometers and then at the end of the freeze to ensure that the freeze plateau has progressed as expected. As a continuing check on the overall purity of the metal sample contained in the fixed-point cell, melting and freezing curves should be obtained every 6 months and compared with those obtained previously.

In assigning a temperature value to a realization of a freezing-point cell, corrections must be applied for the depth of immersion (ℓ) of the thermometer sensing element below the surface of the metal ($dt/d\ell = 2.2 \times 10^{-3}$ °C/m for Sn and 2.7×10^{-3} °C/m for Zn) [1]. Also, if the pressure (p) over the cell during the measurements is not controlled at 101 325 Pa (1 standard atmosphere), a correction ($dt/dp = 3.3 \times 10^{-8}$ °C/Pa for Sn and 4.3×10^{-8} °C/Pa for Zn) must be made for the difference in pressure [1]. The immersion depth for the SRM cells was 18 cm from the sensor mid-point of the SPRT to the top of the liquid metal surface (distance from the bottom of the graphite re-entrant well to the top of the liquid level is 20.5 cm). The pressure in the cells during use was 101 325 Pa ±27 Pa.

7. Conclusions

The certification process of the freezing-point cells of SRM 1747 and SRM 1748 has shown that the cells contain high-purity (≥99.9999%) metal samples and are acceptable for use as a defining fixed points of the ITS-90. Direct comparisons of the SRM cells with the appropriate laboratory standard

have shown that the SRM cells contain metal samples of slightly lower purity than the laboratory standard. A copy of a certificate for SRM 1747 and SRM 1748 is given in appendix A and appendix B, respectively.

8. References

[1] H. Preston-Thomas, "The International Temperature Scale of 1990 (ITS-90)," *Metrologia*, Vol. 27, pp. 3-10, (1990); *ibid.* p. 107.

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9. Appendix A

Certificate for SRM 1747: Tin Freezing-Point Cell

National Institute of Standards & Technology

Certificate

Standard Reference Material® 1747

Tin Freezing-Point Cell

Serial No. Sn 95-2

Certified Freezing Point (231.928 ± 0.000 39) °C

International Temperature Scale of 1990 (ITS-90)

This Standard Reference Material (SRM) is intended primarily for use as one of the defining fixed points of the International Temperature Scale of 1990 (ITS-90) [1]. The value of 231.928 °C is the temperature assigned to the freezing-point of pure tin [1]. The fixed-point temperature is realized as the plateau temperature of the freezing curve of the high purity tin when it is frozen slowly. SRM 1747 consists of approximately 1071 g of tin with impurities of 0.4 mg/kg contained in a high purity graphite crucible containing a high-purity graphite re-entrant well. The design of the metal fixed-point cells and their assemblies have been described previously [2-5].

An expanded uncertainty ($k = 2$) [6,7] of 0.39 m°C is assigned to Sn 95-2. The Type A standard uncertainty component of 0.15 m °C is the standard deviation of $W(t_{90})$ values of repeated measurements of the laboratory standard cell with a check Standard Platinum Resistance Thermometer (SPRT) [8]. The Type B standard uncertainty components are obtained from the estimated uncertainty of 0.09 m °C in the freezing-point temperature of the laboratory standard calculated from the impurities listed in the metal assay [8], the temperature difference of 0.09 m °C between the SRM cell and the laboratory standard cell as determined from the intercomparison measurements and the uncertainty of 0.014 m°C in those intercomparison measurements [9].

Source of Material: The tin metal (Lot M3821) for this SRM was obtained from Johnson Matthey Co., Spokane, WA 99216.

Notice and Warnings to Users: This fixed-point cell is not of the sealed-cell type. Prior to use, the fixed-point cell should be evacuated and back-filled with an inert gas (Helium or Argon) at least three times. The gas should be controlled to a pressure slightly larger than atmospheric pressure to prevent contaminants from entering the cell.

Temperature studies on the fixed-point cell were performed by G.F. Strouse of the NIST Process Measurements Division.

Statistical consultation was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by J.C. Colbert.

Gaithersburg, MD 20899
Certificate Issue Date: March 31, 1997

Thomas E. Gills, Chief
Standard Reference Materials Program

Instructions for Use: In assigning a temperature value to fixed-point cells for calibration purposes, corrections must be applied for the average depth of immersion (ℓ) of the thermometer sensing element below the surface of the metal ($dt/d\ell = (2.2 \times 10^{-3})$ °C/m). The immersion depth of this cell is 18 cm for SPRTs. Using a NIST-manufactured three-zone furnace, the cell has sufficient immersion to track the hydrostatic-head effect over the lowest 10 cm of immersion. If the pressure (p) over the cell during the measurements is not controlled at 101 325 Pa (1 standard atmosphere) [10], a correction ($dt/dp = (3.3 \times 10^{-8})$ °C/Pa) must be made for the difference in pressure.

Certification Testing: The thermal tests for the certification of this SRM were performed in a manner similar to that described in reference [3]. The cell contains approximately 1071 g of tin obtained from randomly-selected bottles of lot M3821.

The freezing points were prepared using the recommended "induced inner freeze" method [2]. With the metal completely melted, the furnace was set to control at 0.5 °C to 0.75 °C below the freezing-point temperature. The sample cooled and when the SPRT indicated that the cell temperature was within about 10 m °C of the freezing-point value, the cell and the SPRT were withdrawn from the furnace. The cell cooled rapidly and when the SPRT detected recalescence, the cell was replaced in the furnace. In order to freeze a thin mantle of solid around the thermometer well, the SPRT was withdrawn from the cell well, and two fused-silica glass rods, each initially at room temperature, were inserted successively in the well for about 3 min each. Then, the cool SPRT was re-inserted into the cell. Three freezing curves are shown in Figure 1 of this certificate (the region of supercooling and recalescence is not shown, as the curve begins after the reinsertion of the thermometer).

After the metal was slowly and completely frozen, the furnace was set at about 2 °C above the freezing-point temperature to slowly melt the metal over a time of approximately 8 h. Thermometer readings were recorded continuously until the melting was complete. Three melting curves obtained under such conditions are shown in Figure 2 of this certificate.

Following the freezing and melting curve measurements, the plateau temperature of a freezing curve of the test cell was compared directly with that of the standard tin freezing-point cell of the Platinum Resistance Thermometer Calibration Laboratory, using a 25.5 Ω SPRT. Three pairs of measurements, with the SPRT being transferred directly from one cell to the other, were made on each of three separate freezes of the two fixed-point cells being intercompared. Although only the first of the three pairs of measurements on a given freeze of a sample was used to determine the temperature difference between the two cells, the other two measurements on the cells provided information on the progress of the freezes (see Figure 3). (Ideally, the difference between the measurements of each of the pairs would be identical.) Only the first 25 % of the freezing curves were used for the intercomparisons. To remove any bias in the measurements, the cell measured first in the sequence was changed from comparison to comparison. The method of direct comparison is described in detail in reference [9].

The electronic measurement equipment for the direct intercomparisons included an Automatic System Laboratories (ASL) F18[1] resistance-ratio bridge, operating at a frequency of 30 Hz, and a temperature-controlled Tinsley 5685A 100 Ω reference resistor. This reference resistor was maintained at a temperature of (25.00 ± 0.010) °C. Freezing curve and melting curve measurements were made with an excitation current of 1 mA. Direct comparison measurements of the thermometer resistance were conducted at two excitation currents, 1 mA and $\sqrt{2}$ mA with a 25.5 Ω SPRT, to allow analysis of the results at zero-power dissipation. A computer-controlled data acquisition system was used to acquire the ASL F18 bridge readings through the use of an IEEE-488 bus.

[1]Certain commercial materials and equipment are identified in order adequately specify the experimental procedure. Such identification does not imply a recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for this purpose.

REFERENCES

[1] Preston-Thomas, H., "The International Temperature Scale of 1990 (ITS-90)," Metrologia **27**, pp. 3-10 and p. 107 (1990).

[2] Mangum B.W. and Furukawa, G.T., "Guidelines for Realizing the International Temperature of 1990 (ITS-90)," NIST Tech. Note 1265, 190 pages, (1990).

[3] Furukawa, G.T., Riddle, J.L., Bigge, W.R., and Pfeiffer, E.R., "Standard Reference Materials: Application of Some Metal SRMs as Thermometric Fixed Points," Natl. Bur. Stand. (U.S.), Special Publication 260-77, 140 pages, (1982).

[4] Riddle, J.L., Furukawa, G.T., and Plumb, H.H., "Platinum Resistance Thermometry," NBS Monograph 126, U.S. Gov't. Printing Office, Washington, D.C. 20402, (1973).

[5] Mangum, B.W., "Platinum Resistance Thermometer Calibrations," NBS Special Publication 250-22, U.S. Gov't. Printing Office, Washington, D.C. 20402, 364 pages, (1987).

[6] *Guide to the Expression of Uncertainty in Measurement,* ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland, (1993).

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[8] Strouse, G.F. and Tew, W.L., "Assessment of Uncertainties of Calibration of Resistance Thermometers at the National Institute of Standards and Technology," NISTIR 5319, 16 pages, (1994).

[9] Mangum, B.W., Pfeiffer, E.R., and Strouse, G.F. (NIST); Valencia-Rodriguez, J. (CENAM); Lin, J.H. and Yeh, T.I. (CMS/ITRI); Marcarino, P. and Dematteis, R. (IMGC); Liu, Y. and Zhao, Q. (NIM); Ince, A.T. and Çakiroğlu, F. (UME); Nubbemeyer, H.G. and Jung, H.J. (PTB), "Intercomparisons of Some NIST Fixed-Point Cells with Similar Cells of Some Other Standards Laboratories," Metrologia **33**, (1996).

[10] Taylor, B.N., "Guide for the Use of the International System of Units (SI)," NIST Special Publication 811, 1995 Ed., (April 1995).

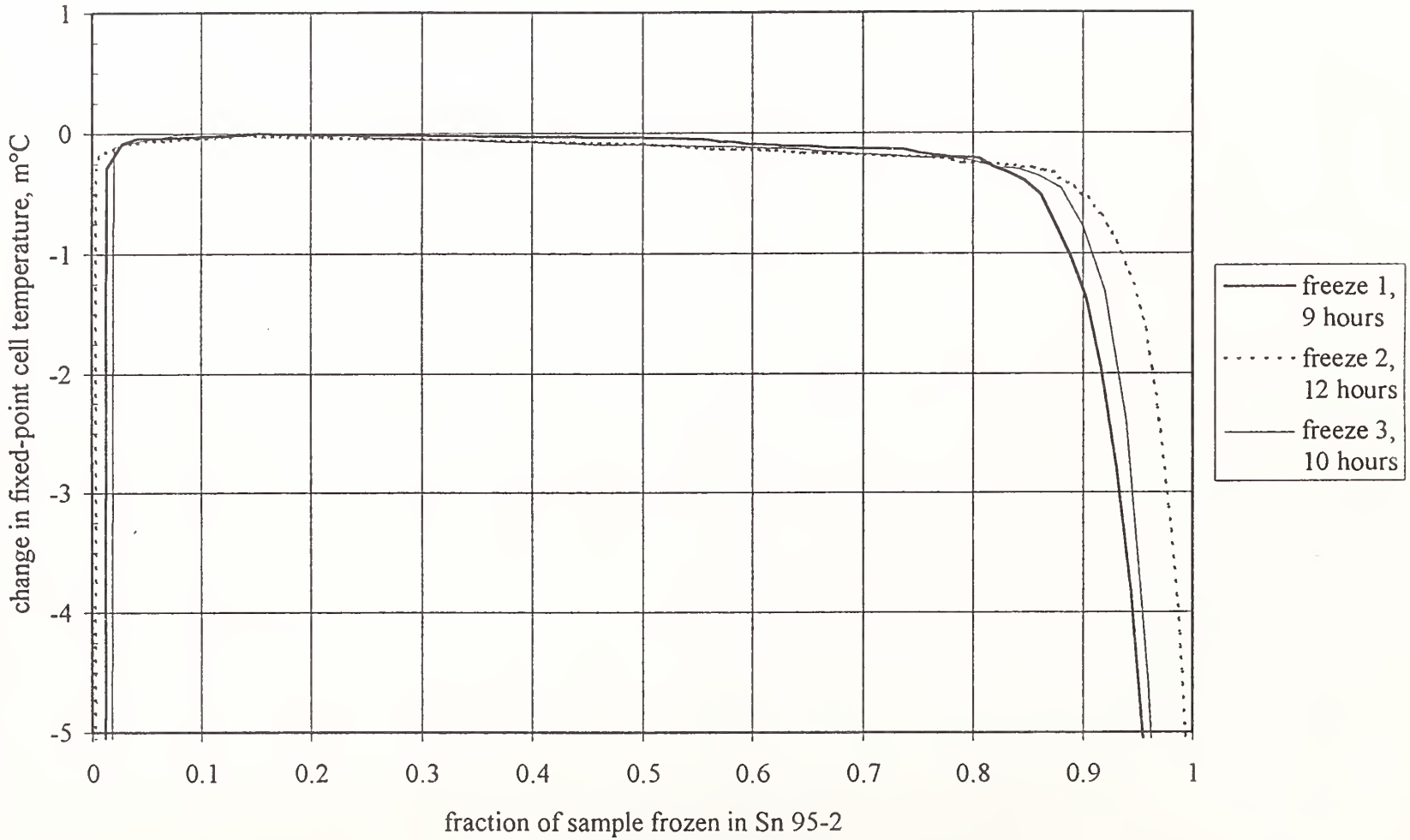

Figure 1. Three freezing curves for the SRM 1747 fixed-point cell Sn 95-2 using the "induced inner freeze" preparation technique.

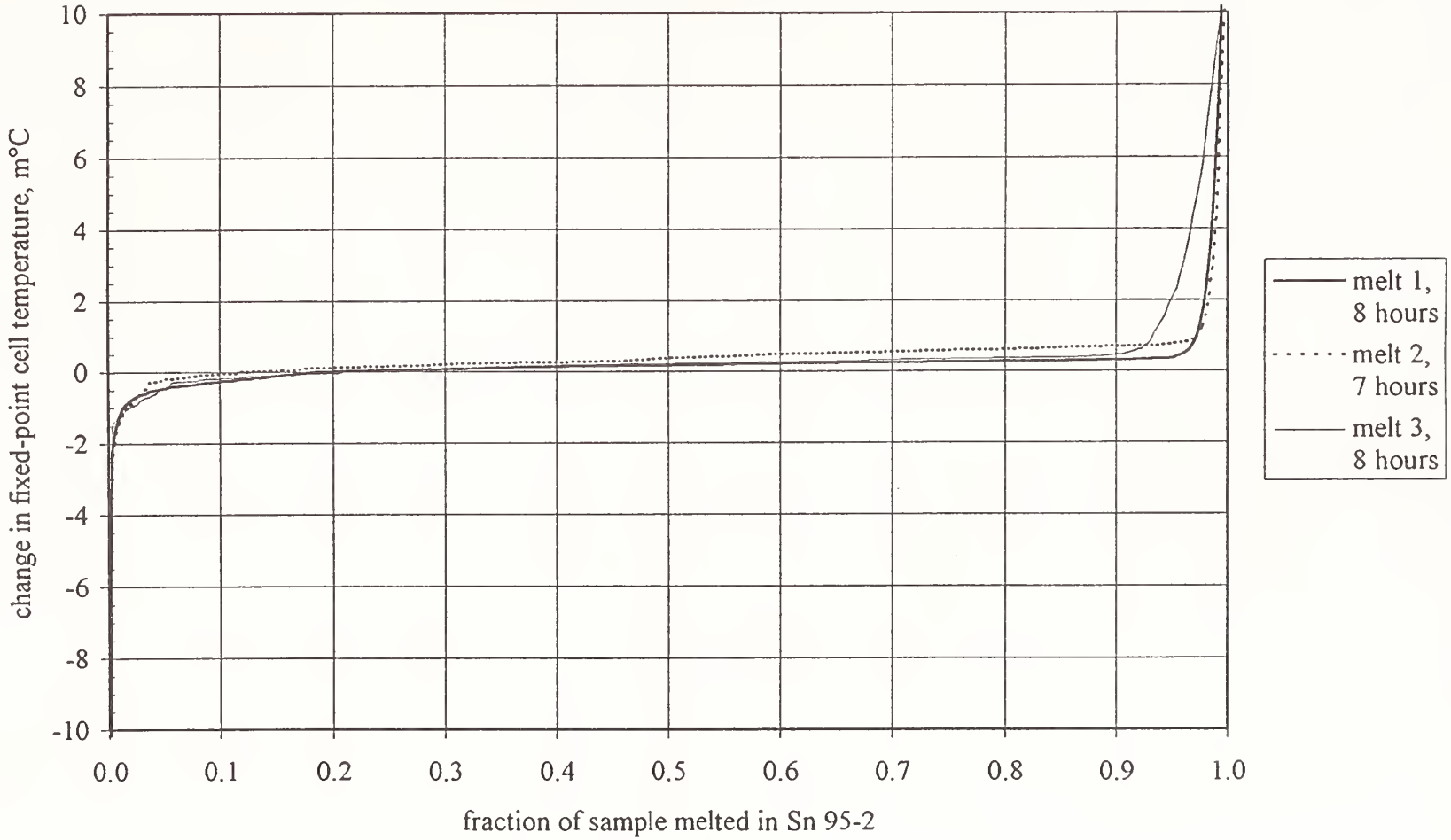

Figure 2. Three melting curves for the SRM 1747 fixed-point cell Sn 95-2 following a slow freeze. Each melt followed the respective slow freeze of Figure 1.

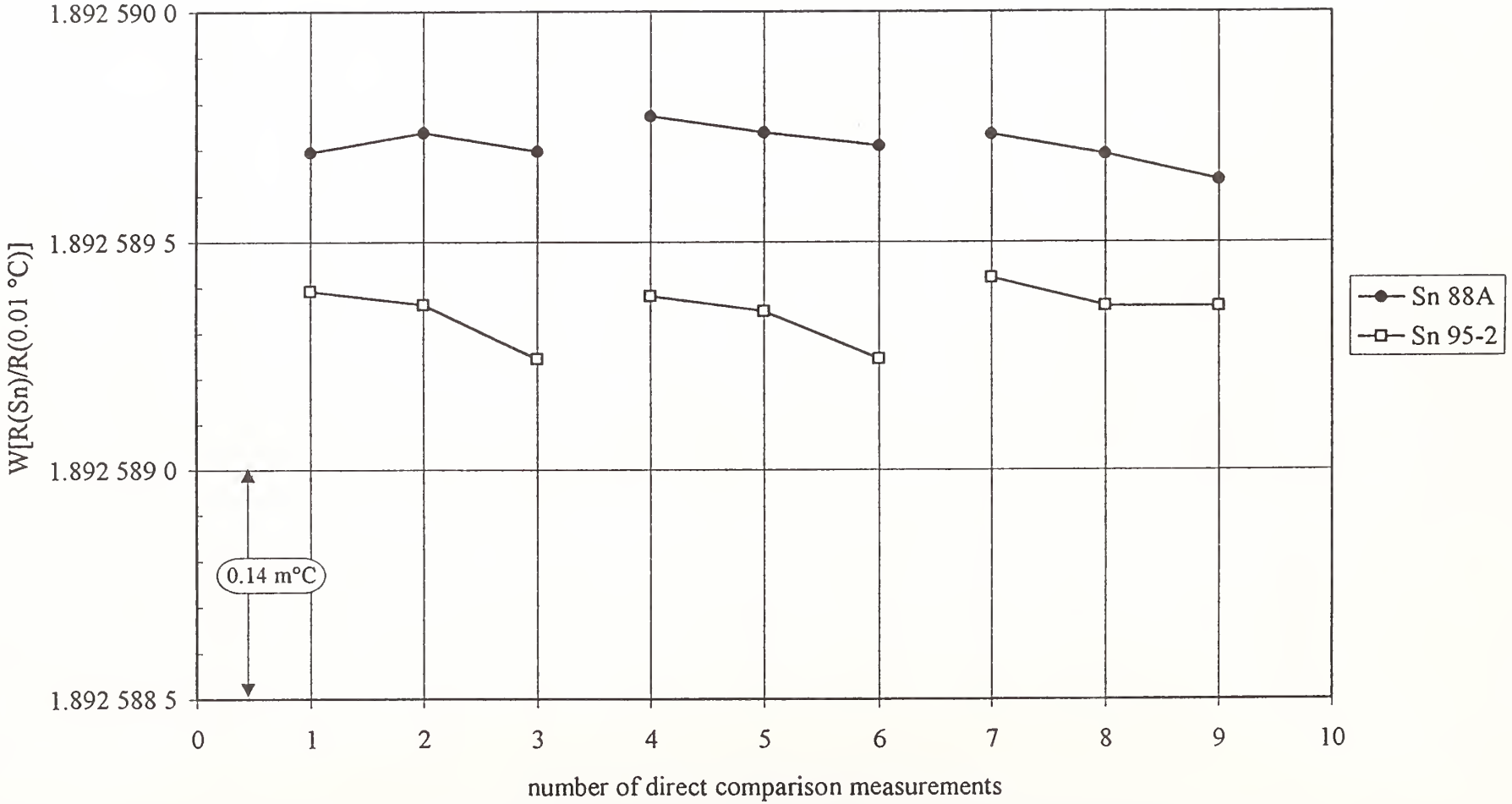

Figure 3. Direct freezing plateau comparison results of SRM 1747 freezing-point cell Sn 95-2 with Sn 88A (laboratory standard). Each set of symbols connected by lines are for the direct comparison measurements made during the simultaneous freezes.

UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
Gaithersburg, Maryland 20899-0001

6 November 1996

NIST
SRMP
Gaithersburg, MD 20899

Subject: SRM 1747 (Tin freezing-point cell): Sn 95-2

Dear Sir:

A direct comparison of your tin freezing-point cell (Sn 95-2) was made against our laboratory standard tin freezing-point cell (Sn 88A). The measurement system included an ASL Model F18 operating at a frequency of 30 Hz with a 100 Ω Tinsley Model 5685 reference resistor and a 25.5 Ω SPRT. The immersion depth of your fixed-point cell is 18 cm for a 25.5 Ω SPRT (distance from top of liquid level to bottom of cell well is 20.5 cm). An expanded uncertainty (k=2) of 0.39 m°C is estimated in the realized value (231.928 °C) of Sn 95-2 to account for the uncertainty in the laboratory standard, the temperature difference between Sn 95-2 and Sn 88A as determined from the direct comparison measurements, and the uncertainty in those intercomparison measurements.

Sincerely,

B. W. Mangum

Dr. B. W. Mangum
Leader, Thermometry Group
Process Measurements Division

NIST

10. Appendix B

Certificate for SRM 1748: Zinc Freezing-Point Cell

National Institute of Standards & Technology

Certificate

Standard Reference Material® 1748

Zinc Freezing-Point Cell

Serial No. Zn 95-5

Certified Freezing Point ($419.527 \pm 0.0011_4$) °C

International Temperature Scale of 1990 (ITS-90)

This Standard Reference Material (SEM) is intended primarily for use as one of the defining fixed points of the International Temperature Scale of 1990 (ITS-90) [1]. The value of 419.527 °C is the temperature assigned to the freezing-point of pure zinc [1]. The fixed-point temperature is realized as the plateau temperature of the freezing curve of the high purity zinc when it is frozen slowly. SRM 1748 consists of approximately 1031 g of zinc with impurities of 0.3 mg/kg contained in a high purity graphite crucible containing a high purity graphite re-entrant well. The design of the metal fixed-point cells and their assemblies have been described previously [2-5].

An expanded uncertainty ($k = 2$) [6,7] of 1.1_4 m °C is assigned to Zn 95-5. The Type A standard uncertainty component of 0.3 m °C is the standard deviation of $W(t_{90})$ values of repeated measurements of the laboratory standard cell with a check Standard Plantinum Resistance (SPRT) [8]. The Type B standard uncertainty components are obtained from the estimated uncertainty of 0.17 m °C in the freezing-point temperature of the laboratory standard calculated from the impurities listed in the metal assay [8], the temperature difference of 0.46 m °C between the SRM cell and the laboratory standard cell as determined from the intercomparison measurements and the uncertainty of 0.022 m °C in those intercomparison measurements [9].

Source of Material: The zinc metal (Lot M3371) for this SRM was obtained from Johnson Matthey Co., Spokane, WA 99216.

Notice and Warnings to Users: This fixed-point cell is not of the sealed-cell type. Prior to use, the fixed-point cell should be evacuated and back-filled with an inert gas (Helium or Argon) at least three times. The gas should be controlled to a pressure slightly larger than atmospheric pressure to prevent contaminants from entering the cell.

Temperature studies on the fixed-point cell were performed by G.F. Strouse of the NIST Process Measurements Division.

Statistical consultation was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by J.C. Colbert.

Gaithersburg, MD 20899
Certificate Issue Date: March 31, 1997

Thomas E. Gills, Chief
Standard Reference Materials Program

Instructions for Use: In assigning a temperature value to fixed-point cells for calibration purposes, corrections must be applied for the average depth of immersion (ℓ) of the thermometer sensing element below the surface of the metal ($dt/d\ell = (2.7 \times 10^{-3})$ °C/m). The immersion depth of this cell is 18 cm for SPRTs. Using a NIST-manufactured three-zone furnace, the cell has sufficient immersion to track the hydrostatic-head effect over the lowest 8 cm of immersion. If the pressure (p) over the cell during the measurements is not controlled at 101 325 Pa (1 standard atmosphere) [10], a correction ($dt/dp = 4.3 \times 10^{-8}$) °C/Pa must be made for the difference in pressure.

Certification Testing: The thermal tests for the certification of this SRM were performed in a manner similar to that described in reference [3]. The cell contains approximately 1031 g of zinc obtained from randomly-selected bottles of lot M3371.

The freezing points were prepared using the recommended "induced inner freeze" method [2]. With the metal completely melted, the furnace was set to control at about 5 °C below the freezing-point temperature permitting the sample to supercool until recalescence was observed with the SPRT. Then, the furnace temperature was set to 0.5 °C to 0.75 °C below the freezing-point temperature and the SPRT was removed from the cell. In order to freeze a thin mantle of solid around the thermometer well, two fused-silica glass rods, each initially at room temperature, were inserted successively in the well for about 5 min each. Then, the cool SPRT was re-inserted into the cell. Three freezing curves are shown in Figure 1 of this certificate (the region of supercooling and recalescence is not shown, as the curve begins after the reinsertion of the thermometer).

After the metal was slowly and completely frozen, the furnace was set at about 2 °C above the freezing-point temperature to slowly melt the metal over a time of approximately 9 h. Thermometer readings were recorded continuously until the melting was complete. Three melting curves obtained under such conditions are shown in Figure 2 of this certificate.

Following the freezing and melting curve measurements, the plateau temperature of a freezing curve of the test cell was compared directly with that of the standard zinc freezing-point cell of the Platinum Resistance Thermometer Calibration Laboratory, using a 25.5 Ω SPRT. Three pairs of measurements, with the SPRT being transferred directly from one cell to the other, were made on each of three separate freezes of the two fixed-point cells being intercompared. Although only the first of the three pairs of measurements on a given freeze of a sample was used to determine the temperature difference between the two cells, the other two measurements on the cells provided information on the progress of the freezes (see Figure 3). (Ideally, the difference between the measurements of each of the pairs would be identical.) Only the first 25 % of the freezing curves were used for the intercomparisons. To remove any bias in the measurements, the cell measured first in the sequence was changed from comparison to comparison. The method of direct comparison is described in detail in reference [9].

The electronic measurement equipment for the direct intercomparisons included an Automatic System Laboratories (ASL) F18[1] resistance-ratio bridge, operating at a frequency of 30 Hz, and a temperature-controlled Tinsley 5685A 100 Ω reference resistor. This reference resistor was maintained at a temperature of (25.00 ± 0.010) °C. Freezing curve and melting curve measurements were made with an excitation current of 1 mA. Direct comparison measurements of the thermometer resistance were conducted at two excitation currents, 1 mA and $\sqrt{2}$ mA with a 25.5 Ω SPRT, to allow analysis of the results at zero-power dissipation. A computer-controlled data acquisition system was used to acquire the ASL F18 bridge readings through the use of an IEEE-488 bus.

[1]Certain commercial materials and equipment are identified in order to adequately specify the experimental procedure. Such identification does not imply a recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for this purpose.

REFERENCES

[1] Preston-Thomas, H., "The International Temperature Scale of 1990 (ITS-90)," Metrologia **27**, pp. 3-10 and p. 107 (1990).

[2] Mangum B.W. and Furukawa, G.T., "Guidelines for Realizing the International Temperature of 1990 (ITS-90)," NIST Tech. Note 1265, 190 pages, (1990).

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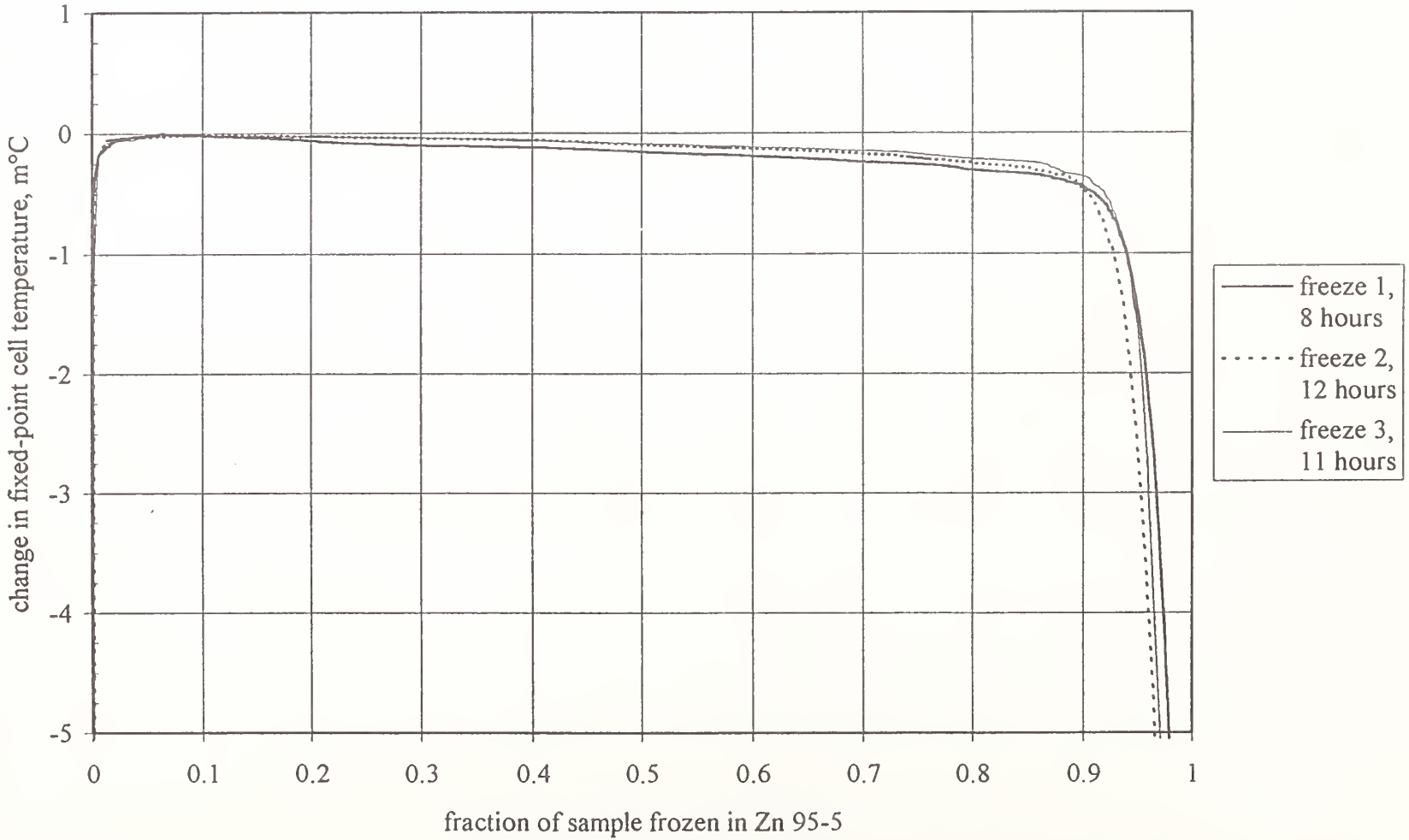

Figure 1. Three freezing curves for the SRM 1748 fixed-point cell Zn 95-5 using the "induced inner freeze" preparation technique.

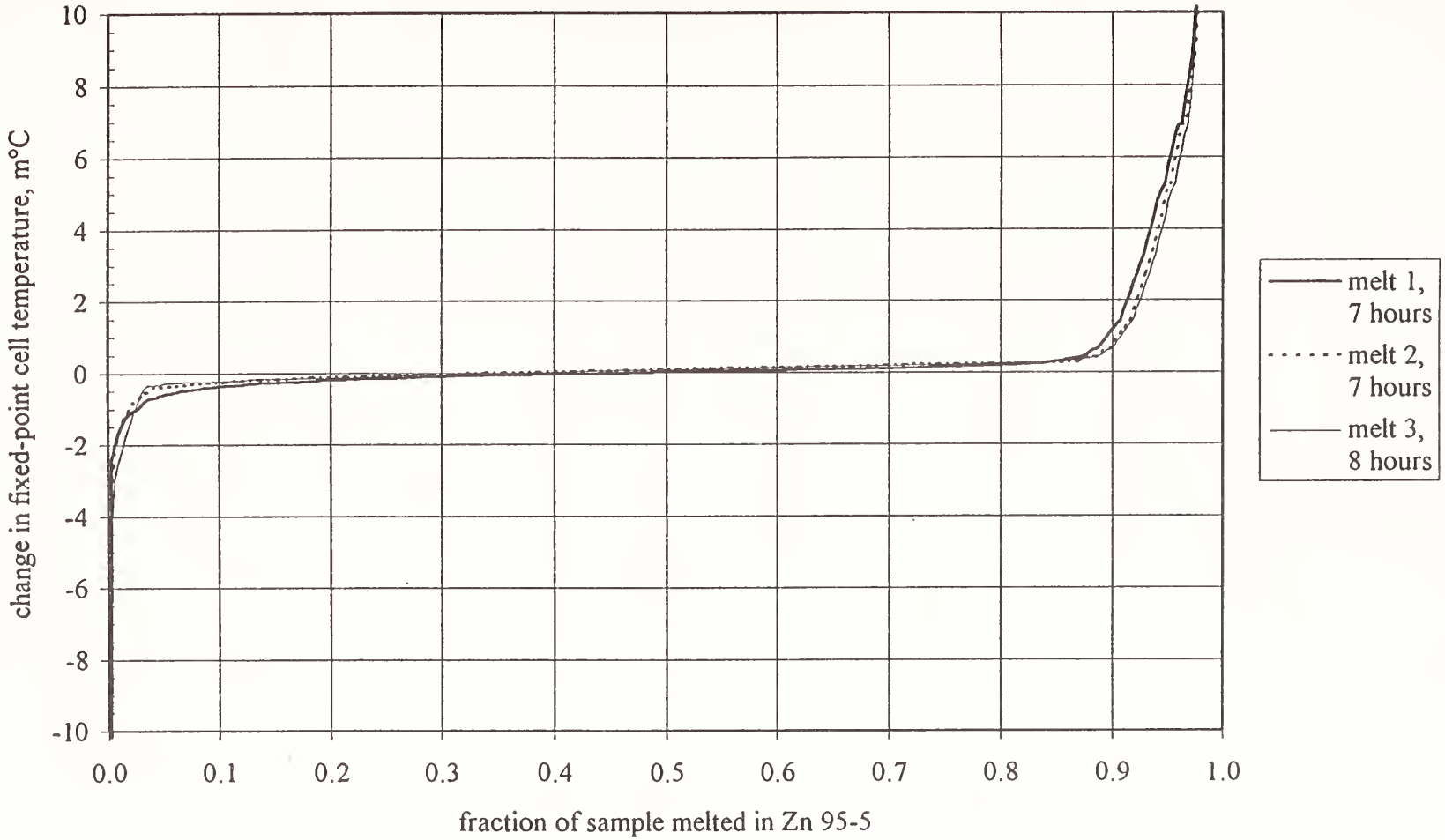

Figure 2. Three melting curves for the SRM 1748 fixed-point cell Zn 95-5 following a slow freeze. Each melt followed the respective slow freeze of Figure 1.

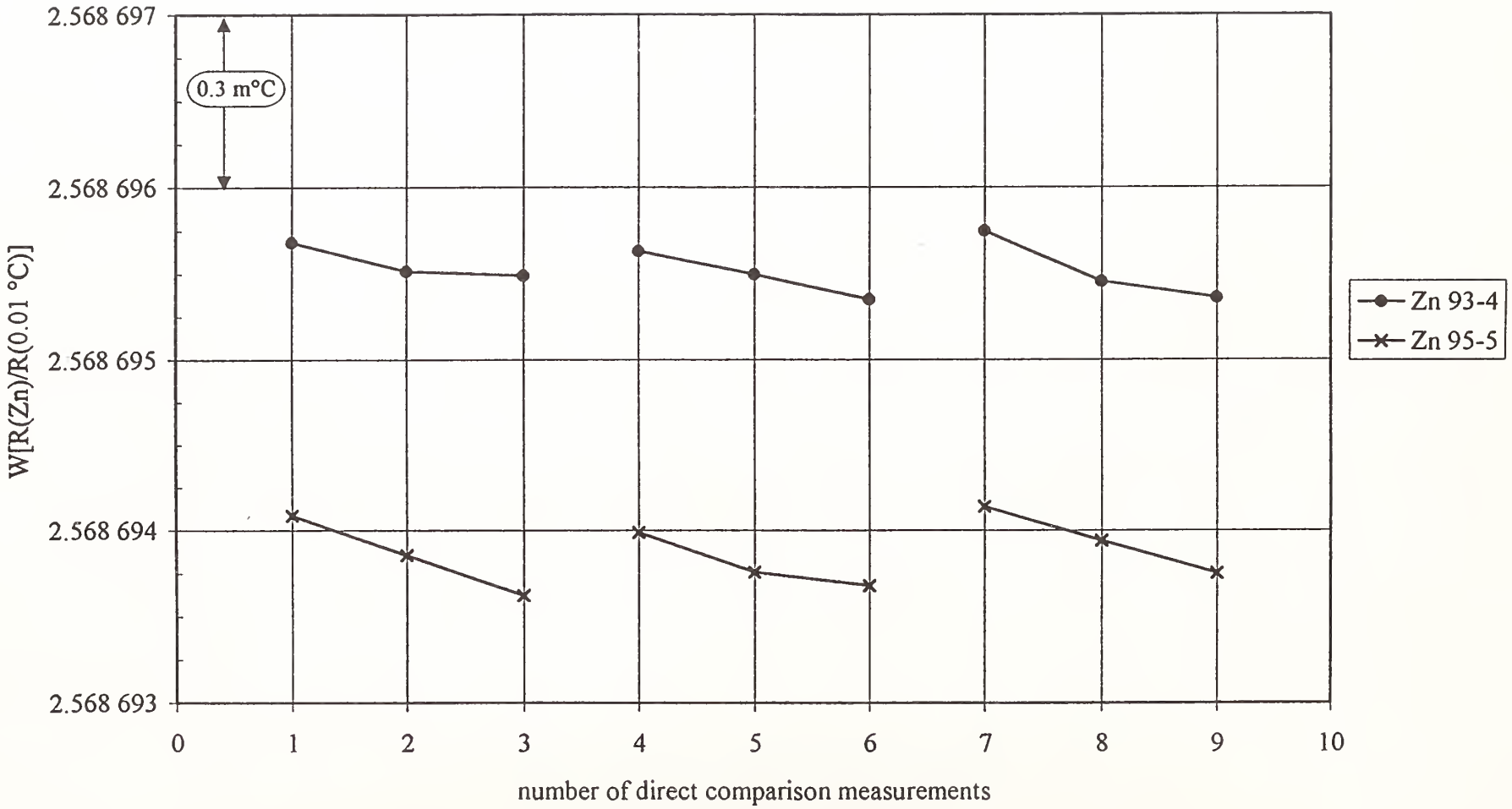

Figure 3. Direct freezing plateau comparison results of SRM 1748 freezing-point cell Zn 95-5 with Zn 93-4 (laboratory standard). Each set of symbols connected by lines are for the direct comparison measurements made during the simultaneous freezes.

UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
Gaithersburg, Maryland 20899-0001

6 November 1996

NIST
SRMP
Gaithersburg, MD 20899

Subject: SRM 1748 (Zinc freezing-point cell): Zn 95-5

Dear Sir:

A direct comparison of your zinc freezing-point cell (Zn 95-5) was made against our laboratory standard zinc freezing-point cell (Zn 93-4). The measurement system included an ASL Model F18 operating at a frequency of 30 Hz with a 100 Ω Tinsley Model 5685 reference resistor and a 25.5 Ω SPRT. The immersion depth of your fixed-point cell is 18 cm for a 25.5 Ω SPRT (distance from top of liquid level to bottom of cell well is 20.5 cm). An expanded uncertainty (k=2) of 1.1_4 m°C is estimated in the realized value (419.527 °C) of Zn 95-5 to account for the uncertainty in the laboratory standard, the temperature difference between Zn 95-5 and Zn 93-4 as determined from the direct comparison measurements, and the uncertainty in those intercomparison measurements.

Sincerely,

B. W. Mangum

Dr. B. W. Mangum
Leader, Thermometry Group
Process Measurements Division

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