



# NIST SPECIAL PUBLICATION 260-132

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

## *Standard Reference Materials:*

**Indium Freezing-Point Standard — SRM 1745**  
**Indium DCS Melting-Point Standard — SRM 2232**

**Gregory F. Strouse**

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National Institute of Standards and Technology  
Technology Administration, U.S. Department of Commerce



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# NIST Special Publication 260-132

*Standard Reference Materials:*

## Indium Freezing-Point Standard — SRM 1745 Indium DCS Melting-Point Standard — SRM 2232

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Thomas E. Gills, Chief  
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# **Standard Reference Material 1745: Indium Freezing-Point Standard and Standard Reference Material 2232: Indium DSC Melting-Point Standard**

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## **Abstract**

The freezing point of indium (156.5985 °C) is a defining fixed point of the International Temperature Scale of 1990 (ITS-90). Realization of this freezing point is performed using a fixed-point cell containing high-purity ( $\geq 99.9999\%$  pure) indium. A single lot of indium ( $\geq 99.9999\%$  pure) constituting Standard Reference Material<sup>®</sup> (SRM<sup>®</sup>) 1745 and SRM 2232 has been evaluated, and certified as suitable for use in the realization of the freezing-point temperature of indium for the ITS-90. Based on results obtained with two fixed-point cells containing random samples of SRM 1745 and one fixed-point cell containing random samples of SRM 2232, the expanded uncertainty ( $k=2$ ) assigned to the freezing-point temperature of the metal is 0.34 m°C. In this document, the methods used for the fabrication of the indium freezing-point cells and for the evaluation of SRM 1745 and SRM 2232 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 author wishes to thank the Standard Reference Materials Program for their support in the development of these new SRMs.

## 1. Introduction

One of the freezing points required to realize the International Temperature Scale of 1990 (ITS-90) is that of indium (156.5985 °C) [1]. This freezing point is realized by using a thermometric fixed-point cell containing high-purity ( $\geq 99.9999\%$  pure) indium metal. Such a fixed-point cell is used for the ITS-90 calibration of standard platinum resistance thermometers (SPRTs) from 0 °C to 157 °C and from 0 °C to 232 °C. To provide evaluated and certified material for this purpose, we have developed a Standard Reference Material<sup>®</sup> (SRM<sup>®</sup>), the Indium Freezing-Point Standard (SRM 1745). Additionally, from the same lot of metal, the melting-point of the Indium sample was evaluated and certified as a Differential Scanning Calorimeter (DSC) Melting-Point Standard (SRM 2232).

The certification of SRM 1745 and SRM 2232 was performed by evaluating three fixed-point cells (SRM 1745 cells designated In 96-4 and In 96-5 and the SRM 2232 cell designated In 96-6) containing random samples of the single lot of high-purity ( $\geq 99.99999\%$  pure) metal constituting the two SRMs. The certification included the evaluation of freezing and melting curves and the direct comparison with the laboratory indium freezing-point reference cell (In 96-3) in the NIST Platinum Resistance Thermometry (PRT) Laboratory. Using the three fixed-point cells, these methods of evaluation were used to confirm the purity and the freezing-point temperature of SRM 1745 and melting-point temperature of SRM 2232 relative to the indium (99.99999% pure) used in In 96-3. The fabrication of the indium fixed-point cells used to certify SRM 1745 and SRM 2232 are described and the results from the certification of SRM 1745 and SRM 2232 are given.

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 cells 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.

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

### 2.1 SRM Sample

A 24 kg lot (S2739) of high-purity (99.99999% pure) In metal to be used for SRM 1745 and SRM 2232 was purchased from Arconium, Providence, Rhode Island. The metal was packaged in two forms. The SRM 1745 metal is in 10 g ingots with each ingot sealed in an Ar atmosphere in a Mylar bag. The SRM 2232 metal is in nominally 1 g pieces with each piece sealed in an Ar atmosphere in a Mylar bag. The Arconium emission spectrographic assay of the In (Appendix A) shows the total impurity level to be 0.1 µg/g (0.1 parts per million), resulting from 0.05 µg/g of Sn,

0.02  $\mu\text{g/g}$  of Pb, 0.005  $\mu\text{g/g}$  of Fe, 0.004  $\mu\text{g/g}$  of Ni, 0.004  $\mu\text{g/g}$  of Al, 0.01  $\mu\text{g/g}$  of Na and 0.007  $\mu\text{g/g}$  of Si.

## 2.2 Indium Fixed-Point Cell

Three thermometric fixed-point cells (In 96-4, In 96-5 and In 96-6) were constructed to certify the indium metal for use as an ITS-90 freezing-point standard. Each cell contained 1190 g of the high-purity metal from randomly selected bags of lot S2739.

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 a 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 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  $101\,325\text{ Pa} \pm 27\text{ Pa}$ .

The high-purity ( $\geq 99.9999\%$  pure) graphite pieces (crucible, well, cap and heat shunts) 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  $149\text{ cm}^3$ .

The fixed-point cell assembly of the In 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 Assembling of the Fixed-Point Cell

Any handling procedure of high-purity material is apt to introduce contamination. The small ingot form is convenient for handling and filling during freezing-point cell construction, while a solid cylinder sample may require cutting and cleaning. By using one-time use polyethylene gloves, every

possible effort was made to maintain the purity of the indium and other fixed-point cell components that come in contact with the indium.

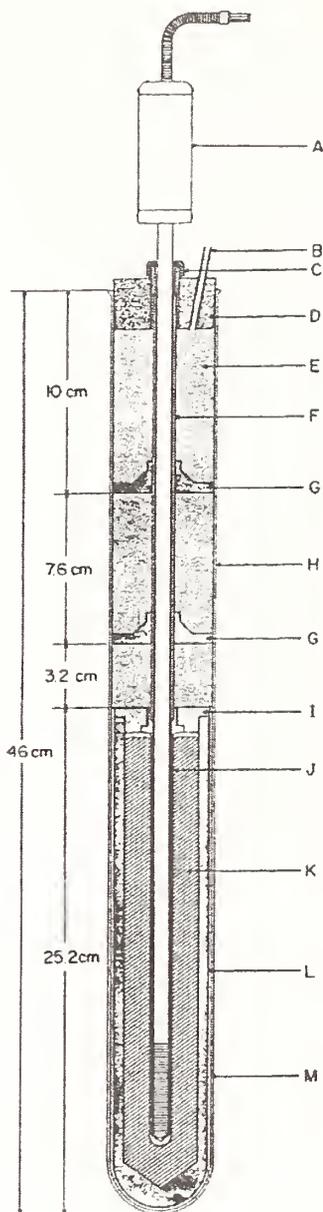


Figure 1. A schematic of an SRM freezing-point cell showing: (A) a 25.5  $\Omega$  SPRT; (B) fill tube to inert gas (Ar or He) supply and pressure gauge; (C) thermometer gas seal (a modified Swagelok fitting with a silicone rubber O-ring); (D) silicone rubber stopper; (E) thermal insulation (1.2 cm thick 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.

Prior to filling the graphite crucible with the indium metal ingots the graphite crucible assembly (crucible, cap and re-entrant well) was placed in a silica-glass furnace tube and "baked-out" at approximately 600 °C under vacuum overnight. This "bake-out" of the graphite was a final purification to remove hydrocarbons and other contaminants that might have been present from the fabrication process. The vacuum system used during the fabrication of the indium freezing-point cells is described in Ref. 2.

This silica-glass furnace tube used in the assembly process is a 4.8 cm o.d. test tube with a silica-glass pumping tube placed near the top of the furnace tube to allow for evacuation and filling with purified argon during use. The open end of the furnace tube is sealed with either a solid silicone-rubber stopper or a stopper with a vacuum seal that allows a silica-glass push rod to be used for pushing the graphite well into place.

After the graphite assembly was heated and cooled to ambient under vacuum, the furnace tube was purged with purified argon and the graphite assembly 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 1 hour; (4) rinsed with copious amounts of distilled water, and then (5) dried. After each use ("bake-out" or "fill"), the silica-glass furnace tube was cleaned.

High-purity argon gas is necessary during the construction of the indium fixed-point cell. The gas purification system for argon described in Ref. [2] was designed to remove any hydrocarbons, oxygen, or water that would contaminate the indium.

In order to introduce 1190 g of indium into the crucible and insert the graphite re-entrant well, two fillings were required. The indium ingots were placed directly into the graphite crucible. Approximately 930 g of the indium ingots could be put into the graphite crucible for the first "fill." The graphite crucible with the graphite cap and the first filling were 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 argon to a pressure of 34 kPa. This process of pumping and flushing the system was carried out three times with the system finally under vacuum. Upon the final evacuation, the furnace was turned on and the temperature was brought to 162 °C to melt the indium sample. After about 4 hours the sample was completely melted, and the furnace was allowed to cool to ambient under vacuum. For the second "fill," purified argon was introduced, the graphite crucible was removed from the furnace tube, and the remaining metal was added (about 260 g) to the crucible. 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 furnace tube. A silica-glass push rod extended from the bottom of the graphite re-entrant well through a vacuum seal 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 indium was molten. Finally, using the method described above, the furnace tube was

placed in the furnace, pumped and flushed with purified Ar, and then the metal sample was melted under vacuum. 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. The borosilicate-glass envelope was cleaned in the same manner as described for the silica-glass furnace tube.

### 3. Certification Procedure for SRM 1745 and SRM 2232

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  $\Omega$  standard platinum resistance thermometer (SPRT). The second step in certifying the fixed point cells was to obtain three direct comparisons with the laboratory standard (In 96-3) by simultaneously freezing both the SRM cell and the laboratory standard. An Automatic System Laboratories (ASL) F18 30 Hz ac resistance ratio bridge, with a thermostatically controlled ( $25\text{ }^{\circ}\text{C} \pm 0.01\text{ }^{\circ}\text{C}$ ) Tinsley 5685A ac/dc 100  $\Omega$  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. The freezing point of In was achieved by heating the cell overnight to approximately 5 K above the freezing-point temperature and then setting the furnace temperature about 3 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 0.7 K below the fixed-point temperature of the metal, the check thermometer removed and two fused-silica glass rods were inserted four minutes each into the reentrant well of the cell to induce an inner solid-liquid interface. Finally, 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 triple point of water (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]. Using the total impurity level obtained from the assay of the metal sample and Raoult's Law of dilute solutions, a calculated estimation of the depression in temperature over the first 50% of a freezing curve may be determined. 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 an inappropriate use of Raoult's Law of dilute solutions, an uncertainty in the extrapolation method chosen to derive the temperature depression, an uncertainty in the quantities of the impurities

specified in the emission spectrographic assay, or 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.

### 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 at least 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.

Using a melting curve to determine the purity of the metal 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 a slow melt of the metal sample, following a slow freeze, two liquid-solid interfaces may be 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 three In cells containing the SRM metals were directly intercompared with the NIST laboratory reference cell In 96-3. This was obtained by realizing simultaneous freezes for the two cells in two separate but nearly 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.

## 4. Analysis of Results

### 4.1 Analysis of SRM freezing-point curves

Figures 2 to 4 show the freezing curves for each of the three In 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 three In cells was 12 hours. The time-temperature relationships 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 in 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 each 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 and Raoult's Law of dilute solutions gives a calculated estimation of the depression in temperature of 0.05 m°C. As experimentally determined from the freezing curve plateaus in figures 2 to 4, 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 0.02 m°C, 0.02 m°C, and 0.03 m°C for In 96-4, In 96-5 and In 96-6, respectively.

Comparisons of the average temperature depressions when 50% of the metal of the three fixed-point cells was frozen were made with In 96-3. The average temperature depression from the extrapolated 0% frozen metal (time of recalescence) to the 50% frozen metal of the flat section of the plateaus was 0.02 m°C for In 96-3. The similar temperature depressions in the freezing-point curves for the three cells relative to that of the reference cell indicate that the SRM metal is of similar purity to that of In 96-3.

For the In freezing-point cells containing the SRM metal, the experimentally determined temperature depressions are smaller than the calculated value. Differences between the calculated and the experimentally derived temperature depressions 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.

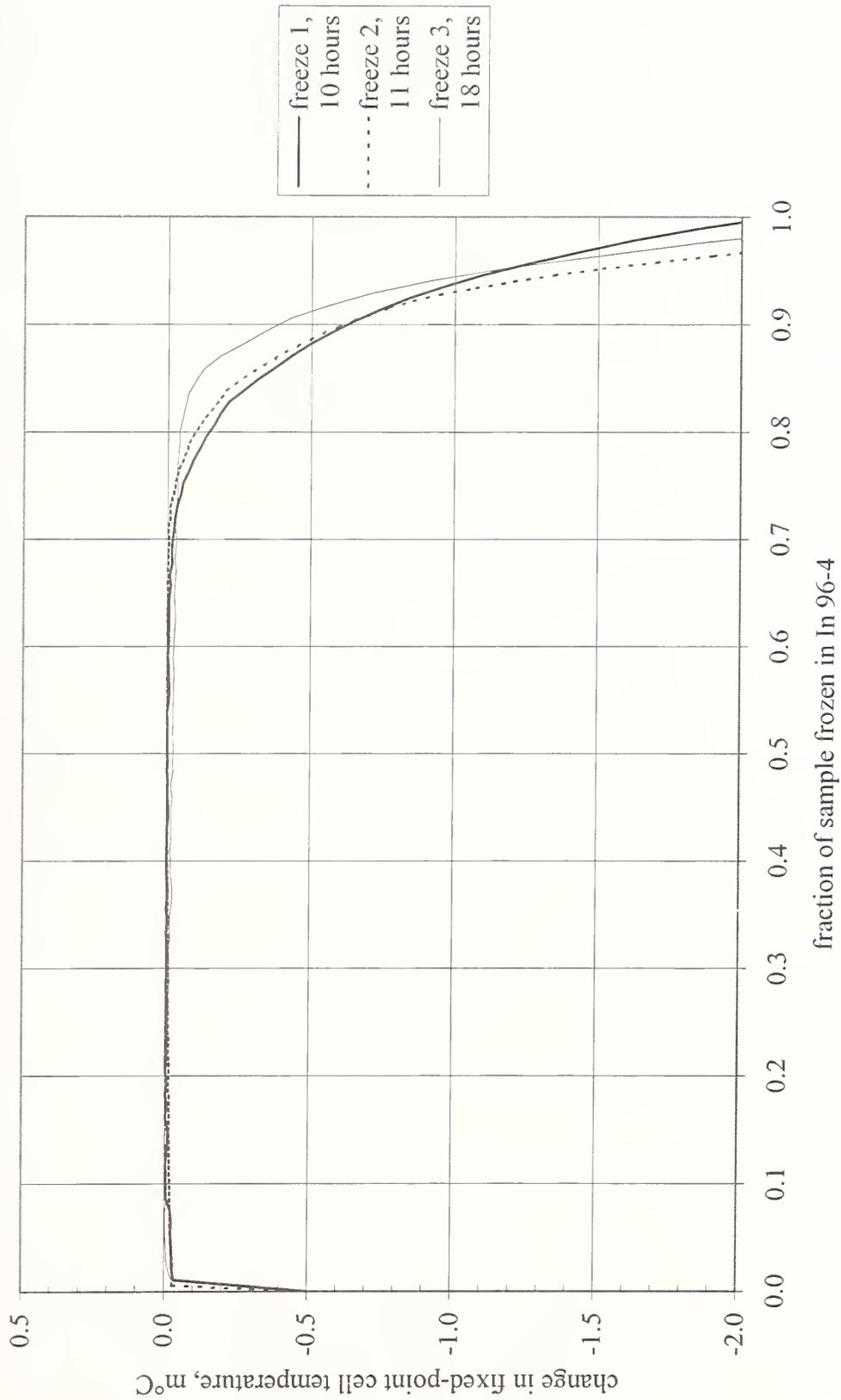


Figure 2. Three freezing curves for the indium fixed-point cell In 96-4 using the "induced inner freeze" preparation technique.

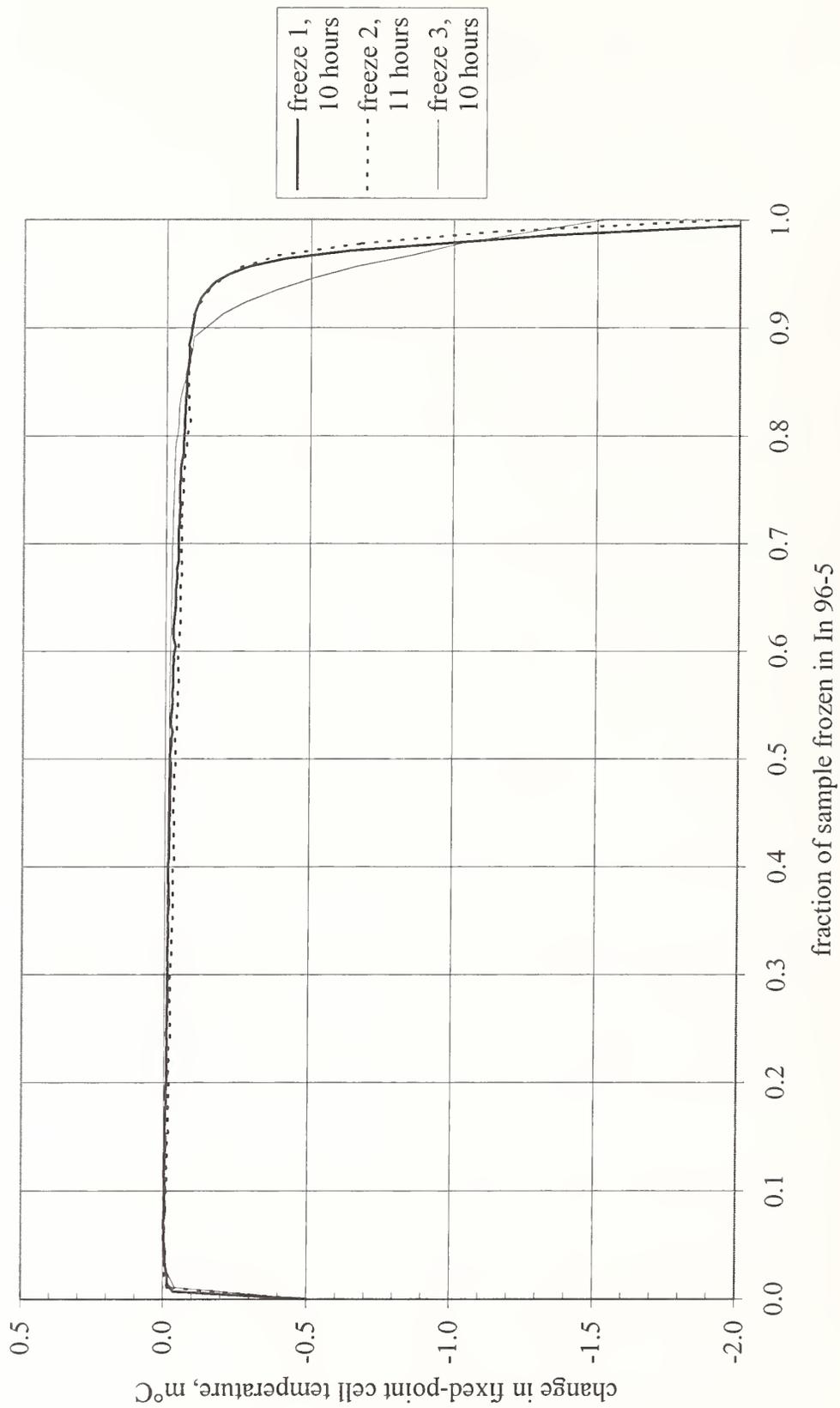


Figure 3. Three freezing curves for the indium fixed-point cell In 96-5 using the “induced inner freeze” preparation technique.

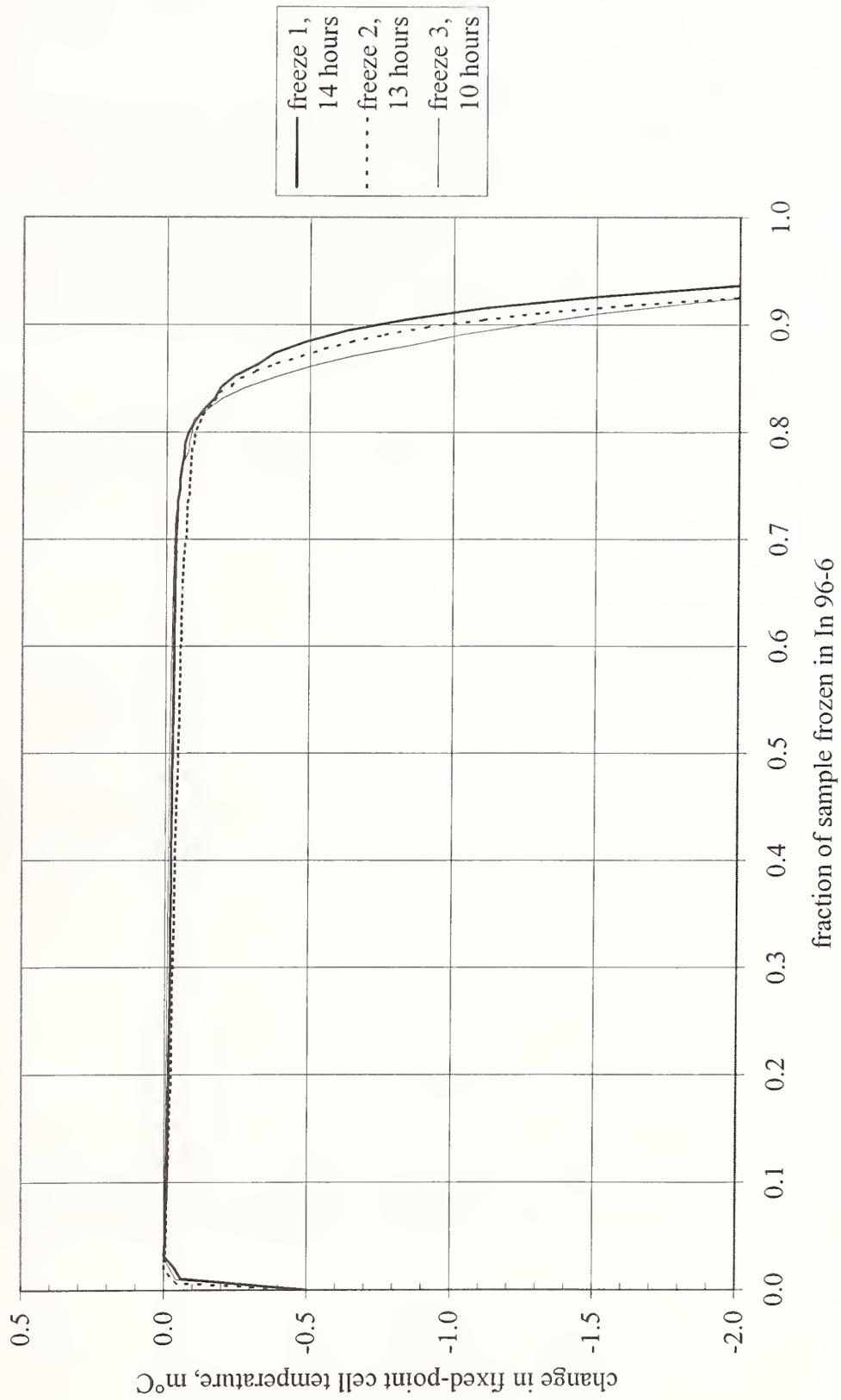


Figure 4. Three freezing curves for the indium fixed-point cell In 96-6 using the "induced inner freeze" preparation technique.

#### 4.2 Analysis of SRM melting-point curves

Figures 5 to 7 show the melting curves for each of the three In 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 was 11 hours. The time-temperature relationships 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 in the figures were normalized so that the SPRT resistance equivalent to 50% melted sample passes through the 0 m°C point on the graph. From the graphs, the average temperature ranges of the melting curves were 0.3 m°C, 0.3 m°C, and 0.3 m°C, for In 96-4, In 96-5 and In 96-6, respectively.

While using a melting curve to determine the purity of the metal is difficult, 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 difference in the liquidus-point temperatures determined from the freezing and melting curves for the In cells was less than 0.1 m°C.

#### 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 (In 96-3) to determine their freezing-point temperatures relative to that of the reference cell. Figure 8 shows the results of the direct comparison of the three In cells with the laboratory standard. The set of matching symbols (open and closed) are for the direct comparison measurements of In 96-X (where X is 4, 5 or 6) compared with In 96-3. The average temperature difference of the first readings of each direct comparison showed that In 96-4, In 96-5 and In 96-6 were 0.01 m°C, 0.02 m°C and 0.02 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

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

The expanded uncertainty  $U$  assigned to the measurements was calculated from the equation: where  $k$  is the coverage factor,  $s$  is the Type A standard uncertainty 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].

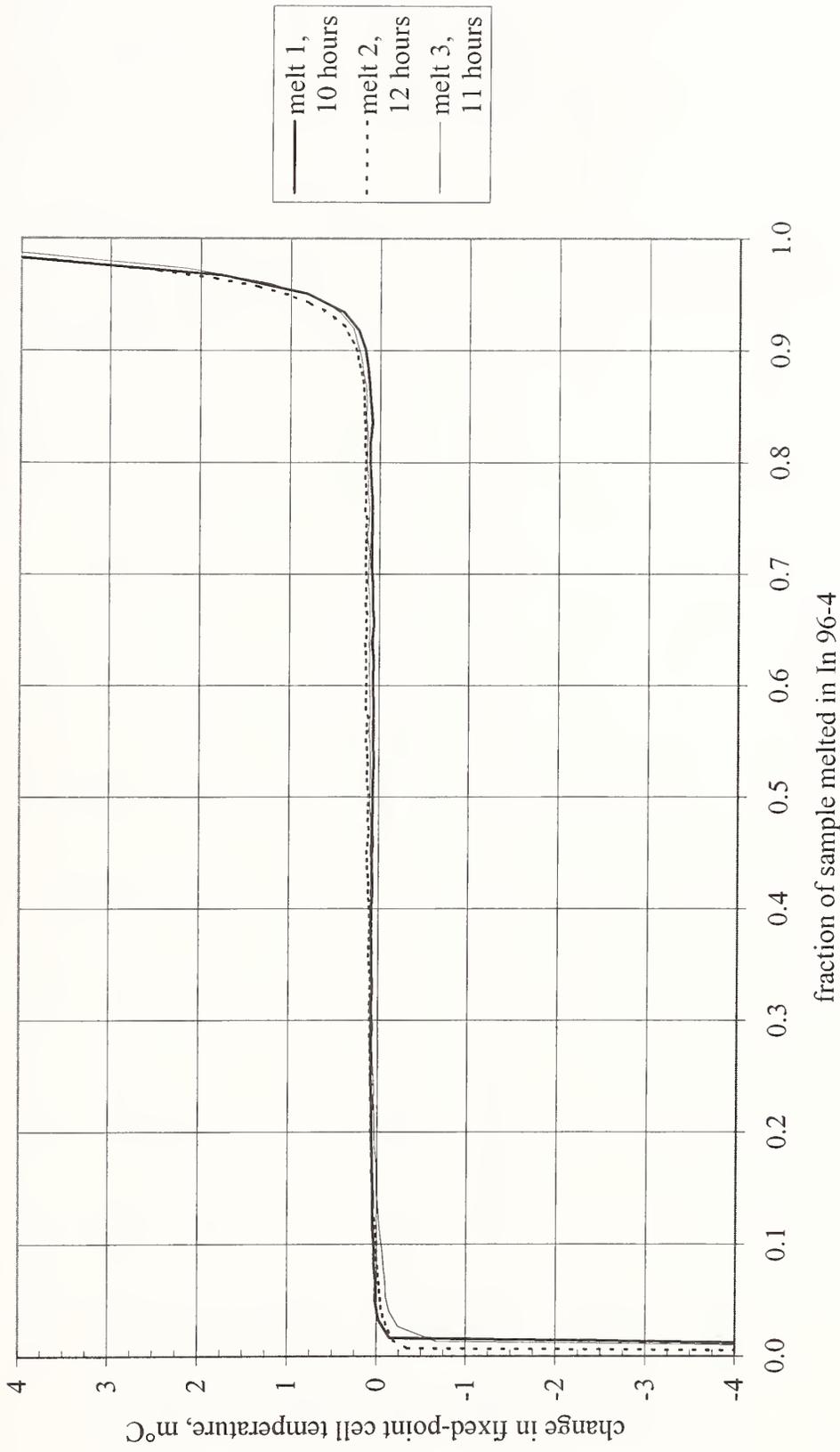


Figure 5. Three melting curves for the indium fixed-point cell In 96-4 following a slow freeze. Each melt followed the respective slow freeze of Figure 2.

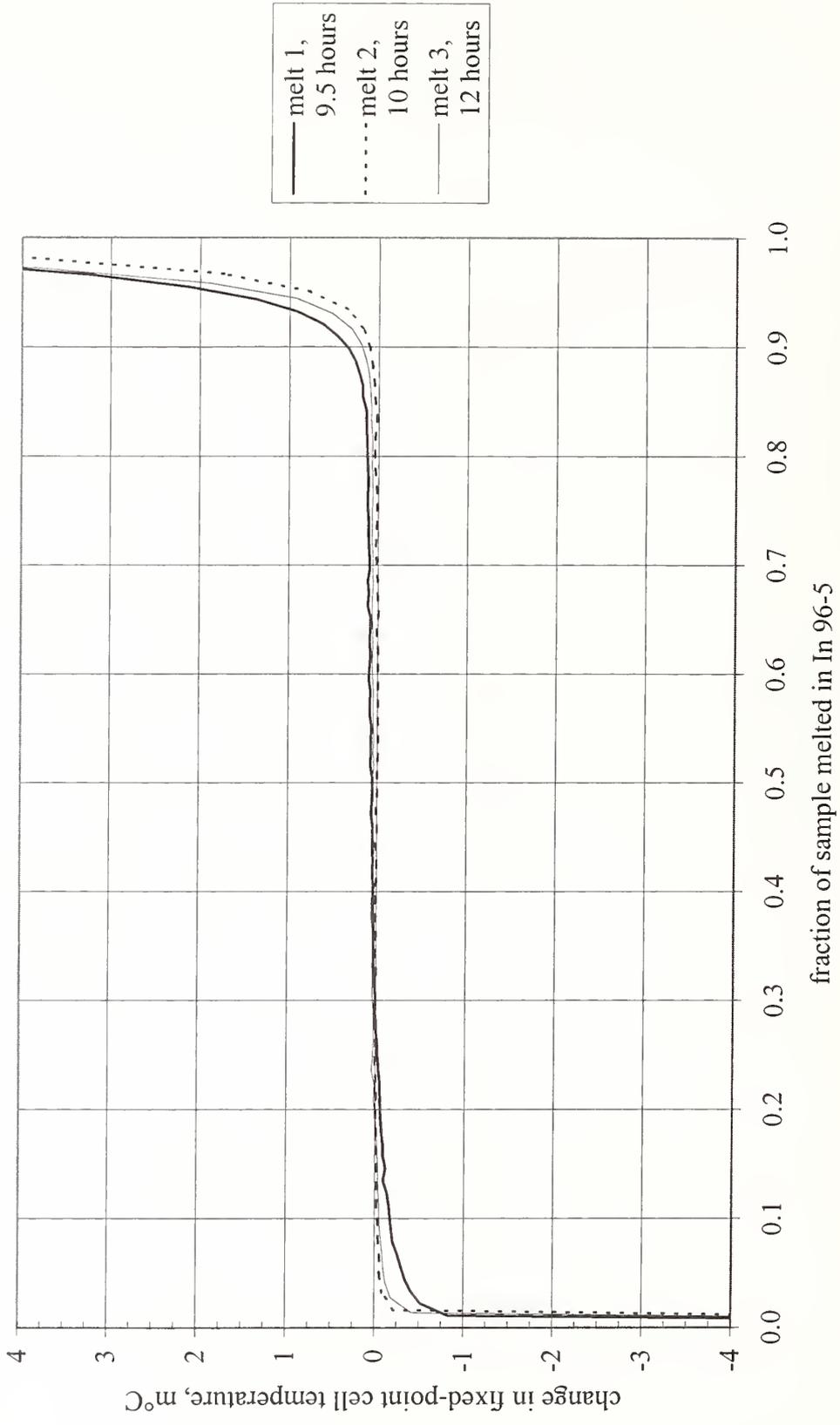


Figure 6. Three melting curves for the indium fixed-point cell In 96-5 following a slow freeze. Each melt followed the respective slow freeze of Figure 3.

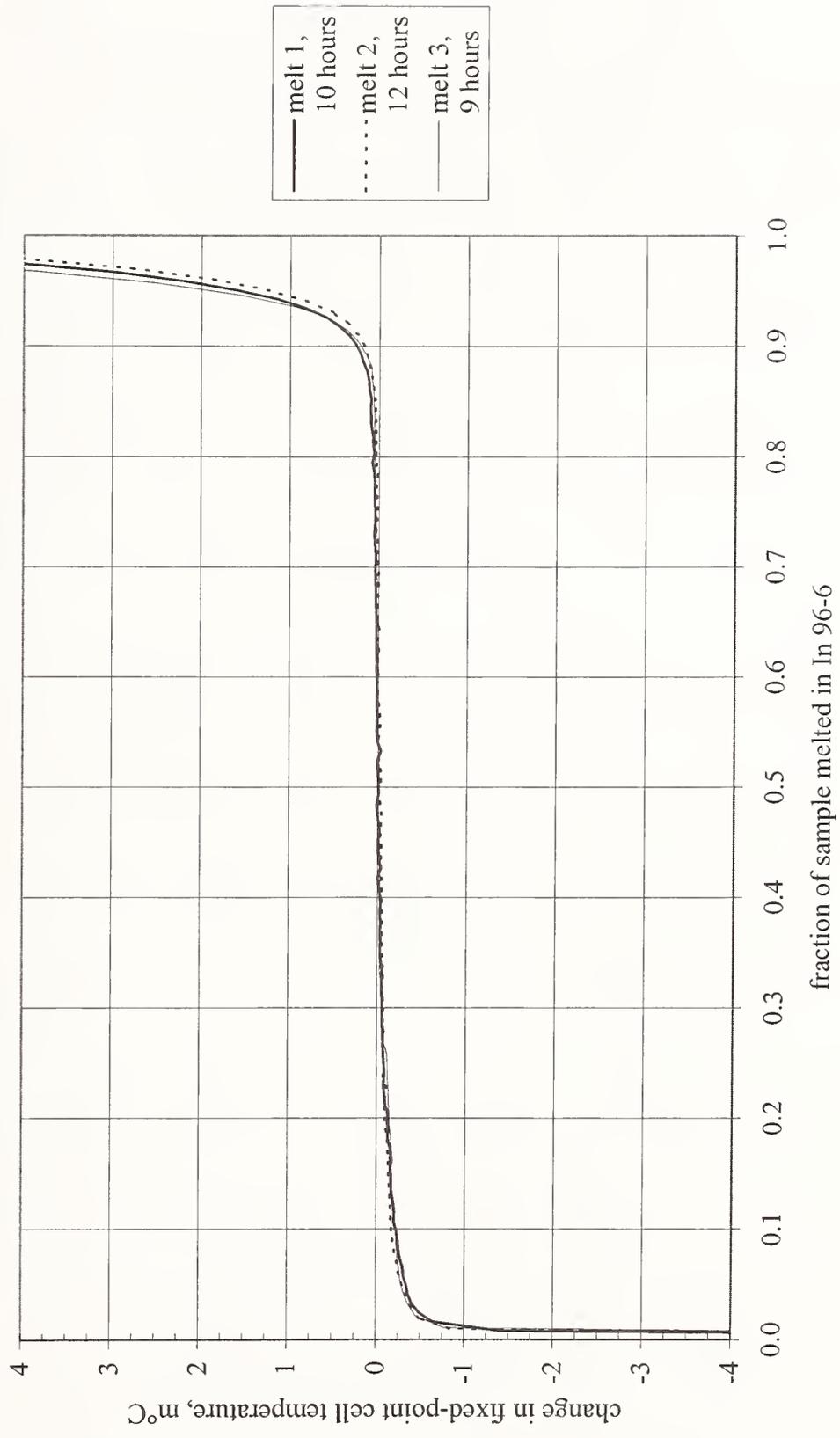


Figure 7. Three melting curves for the indium fixed-point cell In 96-6 following a slow freeze. Each melt followed the respective slow freeze of Figure 4.

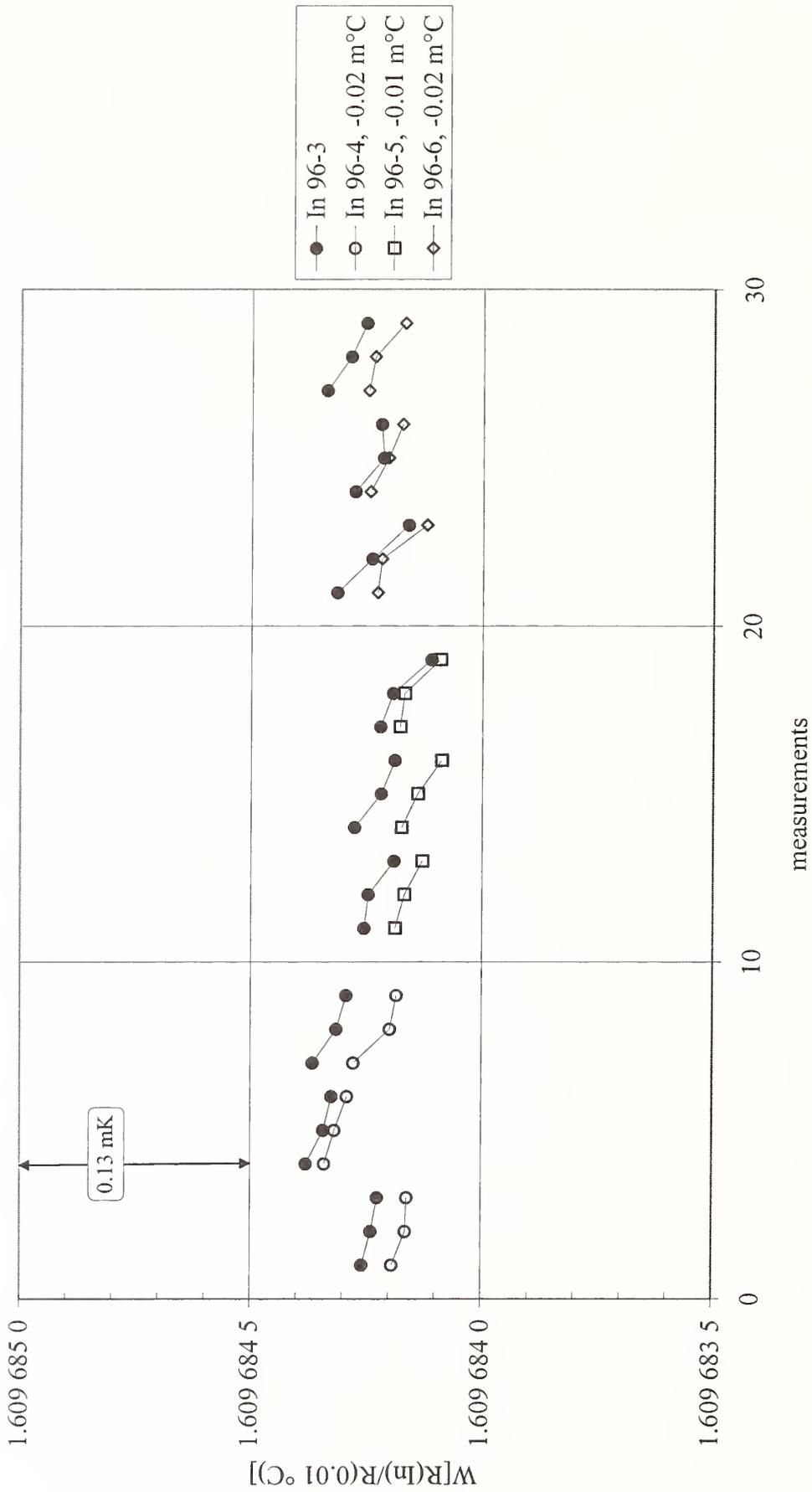


Figure 8. Direct freezing plateau comparison results of In 96-4, In 96-5 and In 96-6 with In 96-3 (laboratory standard). The differences shown in the legend represent the average temperature difference form the first readings of each direct comparison. The set of matching symbols (open and closed) are for the direct comparison measurements of In 96-X (where X is 4, 5 or 6) compared with In 96-3. Each set of symbols (open or closed) connected by lines are for the direct comparison measurements made during simultaneous freezes.

### 5.1 Uncertainty of direct comparison measurements

Many of the systematic effects in the measurement process cancel because the measurements being analyzed are from the direct comparisons of fixed-point cells. There were two possible 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 calculated value of the Type A standard uncertainty for the direct comparison measurements was at most  $0.00_7 \text{ m}^\circ\text{C}$ . The two contributions attributed to the Type A standard uncertainty were calculated to be at most  $0.00_7 \text{ m}^\circ\text{C}$  from the instrumentation and none from handling of the SPRT.

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  $0.00_9 \text{ m}^\circ\text{C}$ . The first contribution coming from the uncertainty in knowing the exact immersion depth of the SPRT due to the uncertainty in the position of the thermometer sensor during measurements gives an uncertainty of  $1.9 \mu^\circ\text{C}$ . The second contribution coming from the uncertainty in knowing the immersion depth of the thermometer due to the uncertainty in the exact fraction of the metal sample frozen gives an uncertainty of  $0.5 \mu^\circ\text{C}$ . The third contribution coming from the uncertainty in the adequacy of immersion of the thermometer to eliminate the thermometer stem conduction during the intercomparisons gives an uncertainty of  $5.7 \mu^\circ\text{C}$ .

The expanded uncertainty ( $k=2$ ) in the intercomparison measurements of the In fixed-point cells containing the SRM metal is  $0.02_7 \text{ m}^\circ\text{C}$ .

### 5.2 Uncertainty assigned to SRM 1745

The Type A, Type B and expanded ( $k=2$ ) uncertainties [10,11] assigned to each of the In freezing-point cells containing the SRM metal is given in Table 1. The Type A standard uncertainty of  $0.16 \text{ m}^\circ\text{C}$  is the standard deviation of  $W(t_{90})$  values of repeated measurements of the laboratory standard In cell with a check SPRT [12]. The Type B standard uncertainty is obtained from the estimated uncertainty of  $0.03 \text{ m}^\circ\text{C}$  in the freezing-point temperature of the laboratory standard calculated from the impurities listed in the metal assay [12], the estimated uncertainty of  $0.03 \text{ m}^\circ\text{C}$  in the freezing-point temperature of the SRM metal calculated from the impurities listed in the metal assay, the temperature difference between the SRM cell and the laboratory standard In cell as determined from the direct comparison measurements (see Section 4.3), and the uncertainty in those direct comparison measurements (see Section 5.1).

Table 1. Estimate of uncertainties assigned to the In freezing-point cells containing the SRM metal.

Freezing-Point Cell	Type A Standard Uncertainty m°C	Type B Standard Uncertainty m°C	Expanded Uncertainty, $k=2$ m°C
In 96-4	0.16	0.06	0.34
In 96-5	0.16	0.06	0.34
In 96-6	0.16	0.06	0.34

### 5.3 Uncertainty assigned to SRM 2232

An additional Type A standard uncertainty must be assigned to the In melting-point temperature for use as a DSC melting-point standard. The average temperature range of the melting curves, following a slow freeze ( $\geq 10$  h), of the fixed-point cell containing SRM 2232 was 0.3 m°C. The estimated expanded uncertainty ( $k=2$ ) assigned to SRM 2232 is 0.45 m°C.

## 6. Application

In assigning a temperature value to realizations of the indium freezing point, corrections must be applied for the depth of immersion ( $l$ ) of the thermometer sensing element below the surface of the metal ( $dt/dl = 3.3 \times 10^{-3} \text{ }^\circ\text{C/m}$ ) [1]. Also, if the pressure ( $p$ ) over the cell during the measurements is not controlled at 101 325 Pa (1 standard atmosphere), a correction ( $dt/dp = 4.9 \times 10^{-8} \text{ }^\circ\text{C/Pa}$ ) must be made for the difference in pressure [1].

For those constructing their own indium freezing-point cell containing SRM 1745, it is necessary to confirm that the purity of the metal was maintained during construction of that cell. This confirmation is made by comparing the freezing and melting curves of the new cell with those shown in figures 2-7. As a continuing check on the overall purity of the indium metal contained in the fixed-point cell, melting and freezing curves should be obtained every 6 months and compared with those obtained previously.

## 7. Conclusions

The evaluation of SRM 1745 for use as an indium freezing-point standard and SRM 2232 for use as a DSC indium melting-point standard has shown that the material is of high-purity ( $\geq 99.999\ 99\%$ ) and is acceptable for use as a defining fixed point of the ITS-90 and has been so certified. Based on the results from the evaluation of the three fixed-point cells containing the SRM metal, the average temperature depression over the first 50% of the freeze is not expected to exceed 0.03 m°C and the average temperature range of melting of the bulk material is not expected to exceed 0.3 m°C. Plateau temperatures of the freezing curves for this material are expected to differ by less than 0.1 m°C from each other. A copy of the certificate for SRM 1745 and SRM 2232 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 1745: Indium Freezing-Point Standard.



# Certificate of Analysis

## Standard Reference Material<sup>®</sup> 1745

### Indium Freezing-Point Standard

Certified Freezing-Point Temperature:  $(156.5985 \pm 0.00034) \text{ }^\circ\text{C}$

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 certified value of  $156.5985 \text{ }^\circ\text{C}$  is the ITS-90 temperature assigned to the fixed point of pure indium. The fixed point is realized as the plateau temperature (or liquidus point) of the freezing curve of the slowly frozen high purity indium. SRM 1745 consists of 200 g of indium in the form of 10 g ingots with each ingot sealed in an argon atmosphere in a Mylar<sup>1</sup> bag.

Based on samples tested, the temperature range of melting of bulk material is not expected to exceed  $0.0003 \text{ }^\circ\text{C}$ . Temperatures of freezing curve plateaus (see Figure 2) for samples of this material are expected to differ by not more than  $\pm 0.0001 \text{ }^\circ\text{C}$  from each other and by not more than  $\pm 0.00034 \text{ }^\circ\text{C}$  from the ITS-90 assigned temperature.

An expanded uncertainty ( $k = 2$ ) of  $0.34 \text{ m }^\circ\text{C}$  is assigned to the freezing point-temperature of SRM 1745. The Type A standard uncertainty component of  $0.16 \text{ m }^\circ\text{C}$  is the standard deviation of  $W(t_{90})$  values of repeated measurements of the laboratory-standard indium cell with a check Standard Platinum Resistance Thermometer (SPRT) [2]. The Type B standard uncertainty components are obtained from: the estimated uncertainty of  $0.03 \text{ m }^\circ\text{C}$  in the freezing-point temperature of the laboratory standard calculated from the impurities listed in the metal assay; the estimated uncertainty of  $0.03 \text{ m }^\circ\text{C}$  in the freezing-point temperature of the SRM metal calculated from the impurities listed in the metal assay; the temperature difference between the SRM cell and the laboratory-standard indium cell as determined from direct comparison measurements; and the uncertainty in those direct comparison measurements.

The indium for this SRM is of high purity, with the total of all elements that affect the freezing-point temperature being less than  $0.1 \text{ mg/kg}$ .

**Expiration of Certification:** The certification of this SRM is valid indefinitely within the measurement uncertainties specified, provided the SRM is used in accordance with the Notice and Warnings to Users section of this certificate.

Temperature measurements of the fixed-point cells were performed by G.F. Strouse of the NIST Process Measurements Division.

The 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: 26 January 1998

Thomas E. Gills, Chief  
Standard Reference Materials Program

**Source of Material:** The indium metal (Lot S2739) for this SRM was obtained from Arconium Specialty Alloys, Providence, RI 02909.

**Notice and Warning to Users:** Because any handling of high purity material is apt to introduce contamination, this SRM is provided in 10 g ingot form in order to minimize the need for handling during freezing-point cell construction. Nevertheless, every possible effort should be made to maintain the purity of this SRM through the use of polyethylene gloves while handling. Also, a clean laboratory environment is essential.

**Instructions for Use:** In assigning a temperature value to realizations of the indium freezing point for calibration purposes, corrections must be applied for the average depth of immersion ( $\ell$ ) of the thermometer sensing element below the surface of the metal ( $dt/d\ell = 3.3 \times 10^{-3} \text{ }^\circ\text{C/m}$ ). Also, if the pressure ( $p$ ) over the cell during the measurements is not controlled at  $1.01325 \times 10^2 \text{ kPa}$  (1 standard atmosphere), a correction,  $dt/dp = 4.9 \times 10^{-8} \text{ }^\circ\text{C/Pa}$ , must be made for the difference in pressure.

**Certification Testing:** The thermal tests for the certification of this SRM were performed on fixed-point cells prepared in a manner similar to that described in reference [3]. Each cell contains approximately 1190 g of indium obtained from randomly selected 10 g ingots of indium.

The freezing points were prepared using the recommended "induced inner freeze" method. With the metal completely melted, the furnace was set at about  $3 \text{ }^\circ\text{C}$  below the freezing point temperature. After supercooling and recalescence had been observed with a  $25.5 \text{ } \Omega$  SPRT in the cell, the thermometer was removed and two fused-silica glass rods, each initially at room temperature, were inserted successively in the well for about 3 min each to induce freezing of a thin mantle of solid metal around the well. The thermometer was then reinserted into the cell and the recording of readings was begun. After equilibrium was established, the temperature of the plateau on the freezing curve was found to vary no more than  $\pm 0.03 \text{ m }^\circ\text{C}$  during the first 50 % of the duration of the freeze. Three freezing curves obtained under such conditions are shown in Figure 1 (the region of supercooling and recalescence is not shown, as the curves begin after the reinsertion of the thermometer); a sample of the data is plotted at greater resolution in Figure 2.

After the metal was slowly and completely frozen in the above manner, the furnace was set at about  $1 \text{ }^\circ\text{C}$  above the freezing-point temperature to slowly melt the metal over a time of approximately 10 h. Thermometer readings were recorded continuously until the melting was complete. Three melting curves obtained under such conditions are shown in Figure 3; some of the same data are plotted at greater resolution in Figure 4.

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 indium freezing-point cell maintained by the NIST Platinum Resistance Thermometer Calibration Laboratory, using a  $25.5 \text{ } \Omega$  SPRT. The method of direct comparison is described in detail in reference [5].

During the freezing and melting curve measurements, an inert environment of argon gas at  $1.01325 \times 10^2 \text{ kPa}$  (1 standard atmosphere) was maintained in the cells.

The electronic measurement equipment included an ASL F18<sup>1</sup> resistance ratio bridge, operating at a frequency of 30 Hz, and temperature controlled Tinsley<sup>®</sup> 5685A  $100 \text{ } \Omega$  reference resistor. This reference resistor was maintained at a temperature of  $(25.000 \pm 0.010) \text{ }^\circ\text{C}$ . 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  $25.5 \text{ } \Omega$  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.

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<sup>1</sup> 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 (1990), *Metrologia* 27, p. 107, (1990).
- [2] 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).
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*It is the responsibility of users of this SRM to assure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: Phone (301) 975-6776 (select "Certificates"), Fax (301) 926-4751, e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov), or via the Internet <http://ts.nist.gov/srm>.*

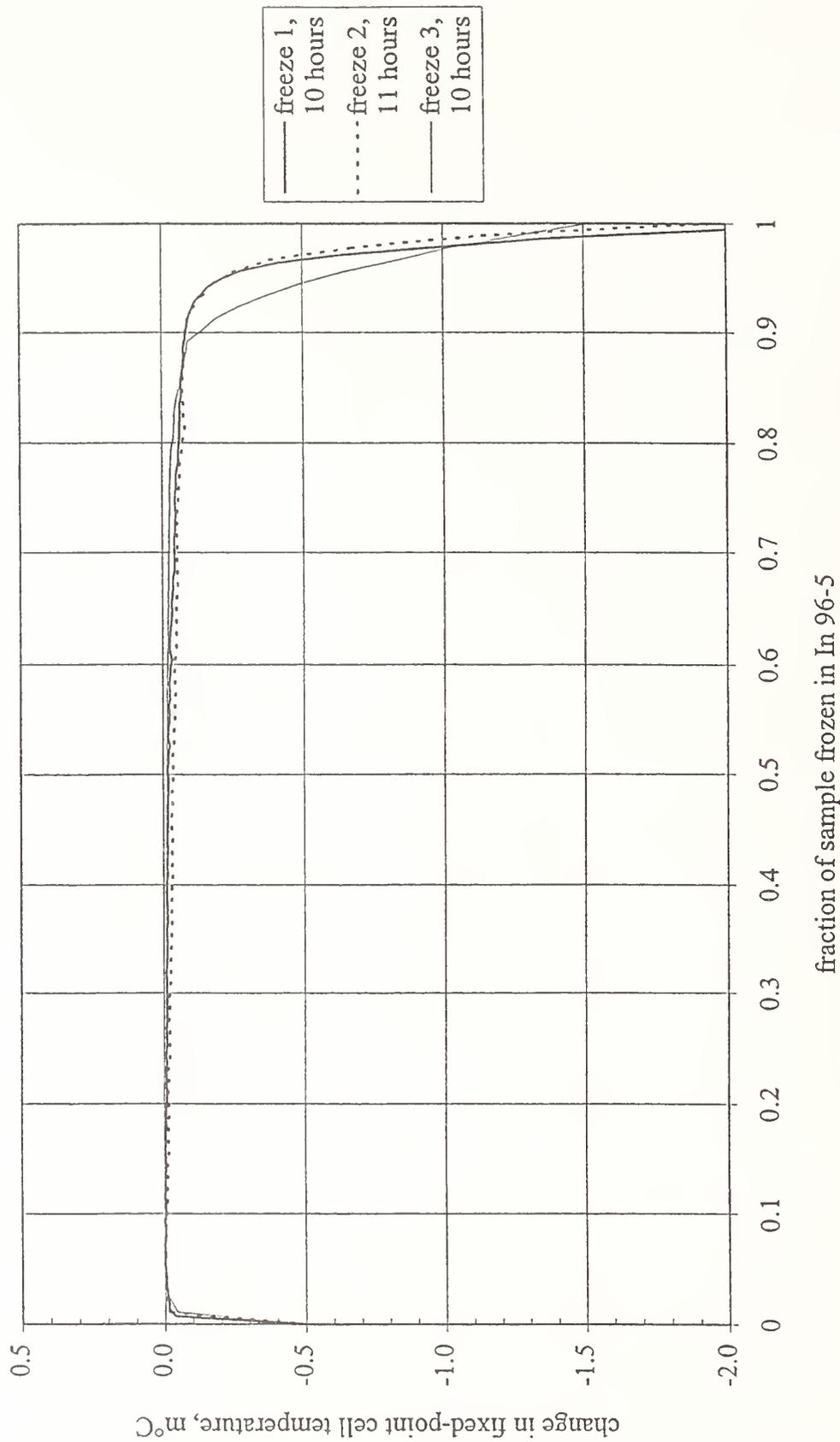


Figure 1. Three freezing curves of SRM 1745 indium using the "induced inner freeze" preparation technique.

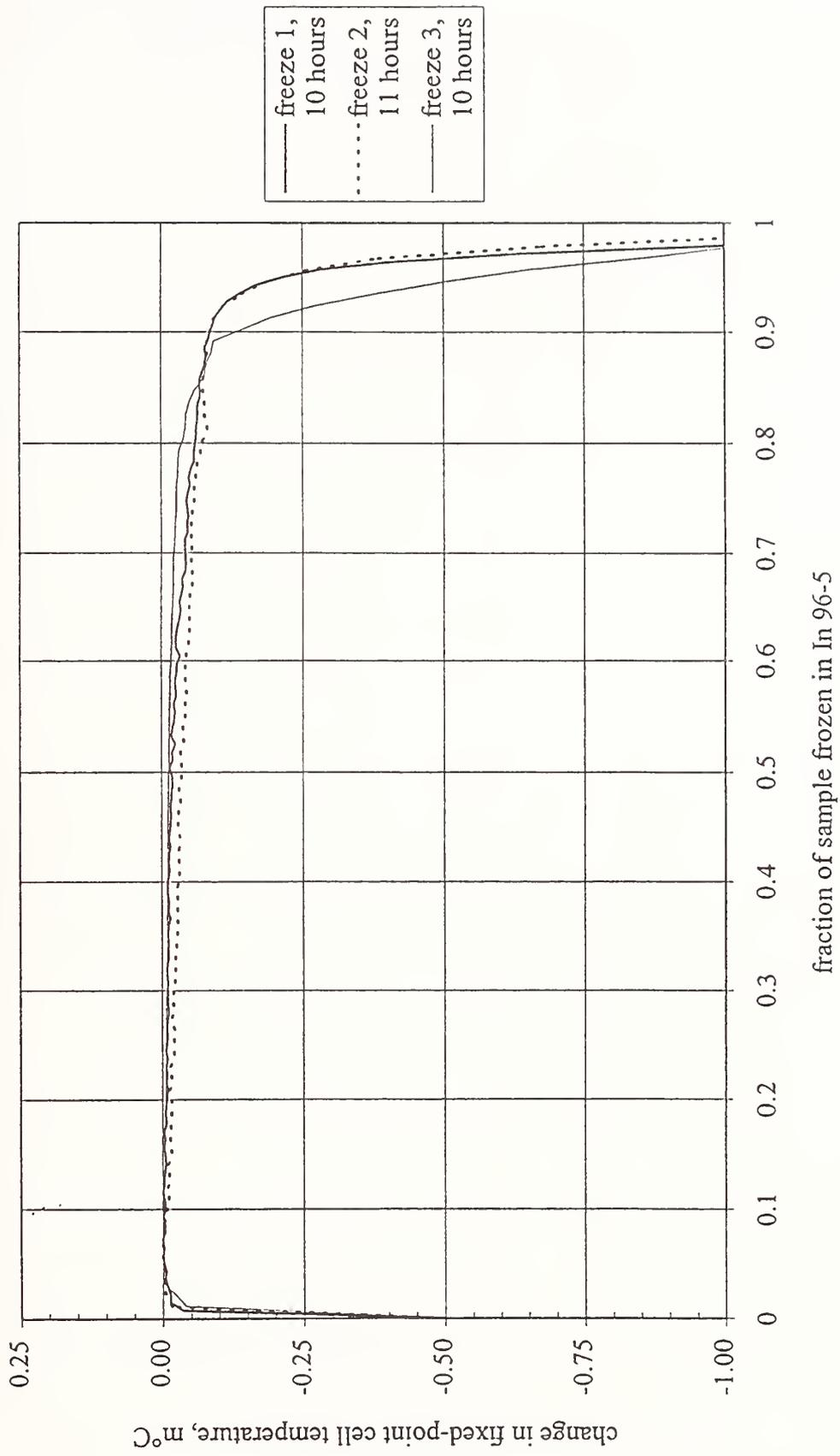


Figure 2. The freezing plateau regions of Figure 1 at greater resolution.

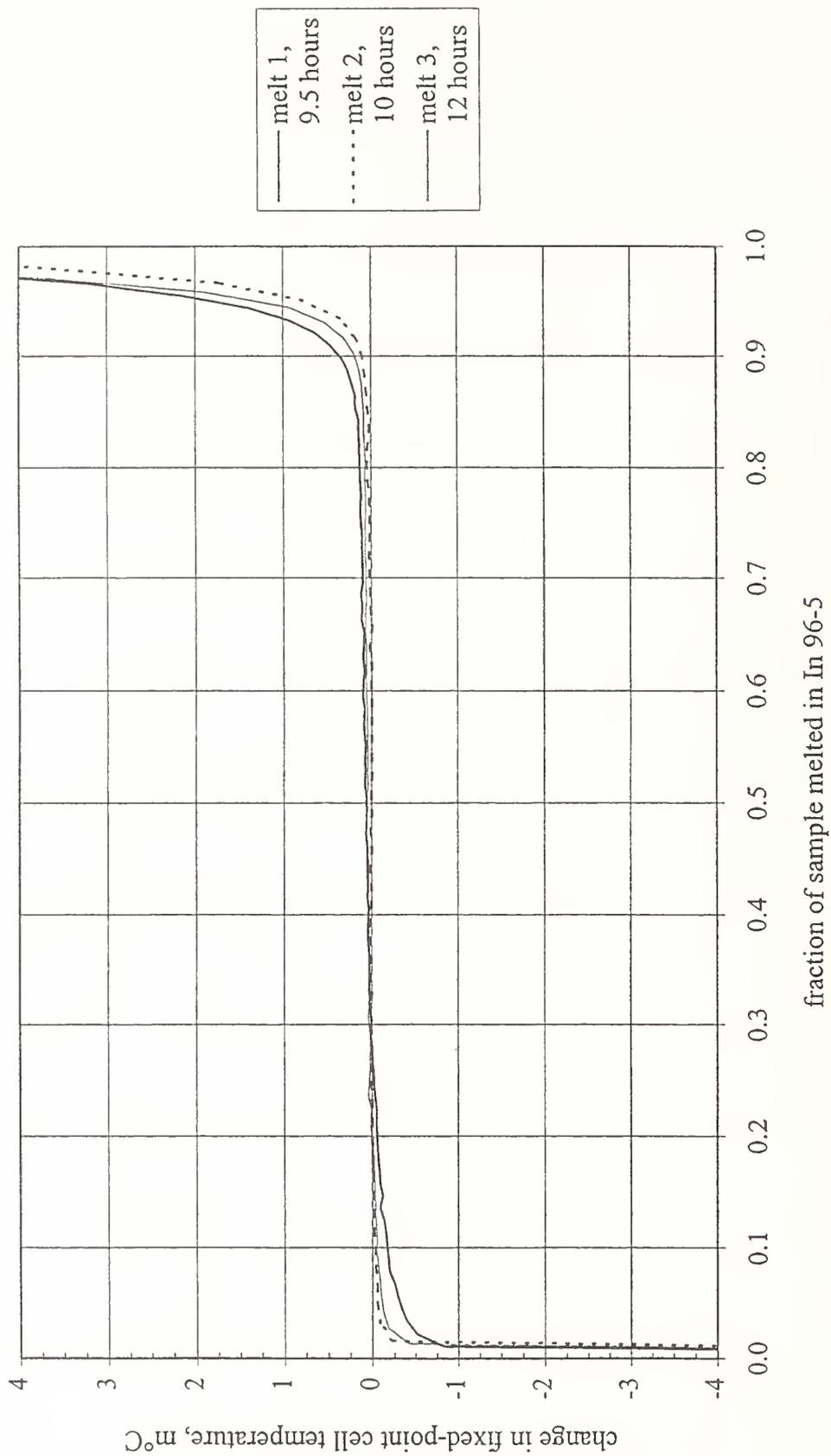


Figure 3. Three melting curves of SRM 1745 indium following a slow freeze. Each melt followed the respective slow freeze of Figure 1.

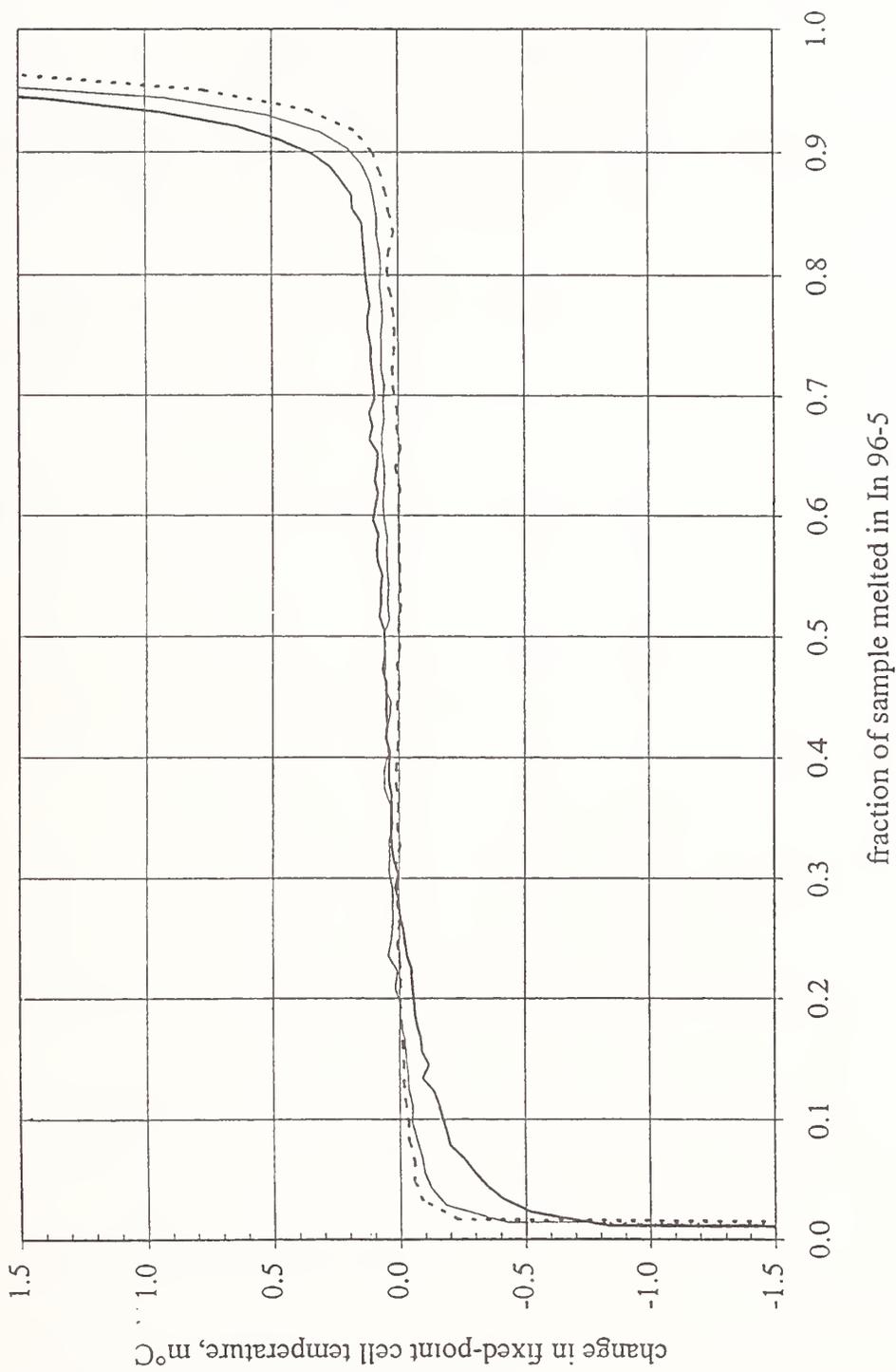


Figure 4. The melting plateau regions of Figure 3 at greater resolution.

## 10. Appendix B

Certificate for SRM 2232: Indium DSC Melting-Point Standard.



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material<sup>®</sup> 2232

#### Indium DSC Calibration Standard Temperature and Enthalpy of Fusion

Standard Reference Material (SRM) 2232 is primarily intended for use in the temperature and enthalpy of fusion calibrations of differential thermal analyzers (DTA), differential scanning calorimeters (DSC), and similar instruments. A unit of this SRM consists of a 1 g piece of indium metal sealed in an argon atmosphere in a mylar bag.

**Certified Temperature of Fusion:** The certified value of 156.5985 °C is the temperature assigned to the melting point of pure indium [1]. The melting point is realized as the plateau temperature of the melting curve of the slowly melted, high purity indium.

Certified Temperature of Fusion (156.5985 ± 0.000 34) °C

Based on samples tested, the temperature range of melting of bulk material is not expected to exceed 0.0003 °C. Temperatures of melting curve plateaus for samples of this material are expected to differ by not more than 0.0001 °C from each other and by not more than 0.000 34 °C from the assigned temperature. The basis for assigning an expanded uncertainty ( $k = 2$ ) of 0.000 34 °C to the temperature of fusion of SRM 2232 is described in [2].

**Certified Enthalpy of Fusion:** The certified enthalpy of fusion value at the DSC onset temperature was determined by performing duplicate measurements on seven SRM 2232 DSC samples. The DSC onset temperature has an expanded uncertainty ( $k = 2$ ) 0.046 °C.

Certified Enthalpy of Fusion (28.51 ± 0.19) J·g<sup>-1</sup>

The uncertainty was calculated as two times the square root of the sum of three components of variance. Component one was the standard deviation of the mean from fourteen measurements of the enthalpy of fusion of indium. Component two was the standard deviation of the mean of fourteen measurements of the enthalpy of fusion of SRM 2220 Tin that were used to calibrate the energy scale. Component three was the variance of the enthalpy certification measurements for SRM 2220, the calibration standard. The variance for SRM 2220 was calculated as the square of one-half the stated uncertainty on the certificate. The basis for assigning an expanded uncertainty ( $k = 2$ ) of 0.19 J·g<sup>-1</sup> to the enthalpy of fusion of SRM 2232 is described in [3].

**Expiration of Certification:** The certification of this SRM is valid indefinitely within the measurement uncertainties specified, provided the SRM is used in accordance with the Notice and Warnings to Users section of this certificate. However, the certification is nullified if the SRM is damaged or contaminated.

The 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.

Richard F. Kayser, Chief  
Physical and Chemical Properties Division

Gregory J. Rosasco, Chief  
Process Measurements Division

Gaithersburg, MD 20899  
Certificate Issue Date: 1 March 1999

Thomas E. Gills, Chief  
Standard Reference Materials Program

Temperature studies on fixed-point cells were performed by G.F. Strouse of the NIST Process Measurements Division. DSC studies were performed by D.R. Kirklin of the NIST Physical and Chemical Properties Division.

## NOTICE AND WARNINGS TO USERS

**Source of Material:** The indium metal<sup>1</sup> (Lot S2739) for this SRM was obtained from Arconium, Providence, RI. The indium is of high purity, with the total of all elements that affect the melting point temperature being less than 0.1 mg/kg.

**Handling of SRM:** Any handling procedures of this high purity material are apt to introduce contamination. Every possible effort should be made to maintain the purity of this SRM.

**Temperature of Fusion Measurements:** The thermal tests for the certification of this SRM were performed on a fixed-point cell prepared in a manner similar to that described in [4]. The cell contains approximately 1190 g of indium obtained from the randomly-selected 1 g pieces of indium of lot S2739.

The freezing points were prepared using the recommended "induced inner freeze" method. With the metal completely melted, the furnace was set at about 3 °C below the freezing point temperature. After supercooling and recalescence had been observed with a 25.5 Ω standard platinum resistance thermometer (SPRT) in the cell, the thermometer was removed and two fused silica glass rods, each initially at room temperature, were inserted successively into the well for about three minutes each to induce freezing of a thin mantle of solid metal around the well. The thermometer was then reinserted into the cell and the recording of readings was begun. After equilibrium was established, the temperature of the plateau on the freezing curve was found to vary no more than 0.000 03°C during the first 50 % of the duration of the freeze. A typical freezing curve obtained under such conditions is shown in Figure 1 (the region of supercooling and recalescence is not shown, as the curve begins after the reinsertion of the thermometer); a sample of the data is plotted at greater resolution in Figure 2.

After the metal was slowly and completely frozen in the above manner, the furnace was set at about 1°C above the freezing point temperature to slowly melt the metal over a time of approximately 10 hours. Thermometer readings were recorded continuously until the melting was complete. A typical melting curve obtained under such conditions is shown in Figure 3.

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 indium freezing point cell of the Platinum Resistance Thermometer Calibration Laboratory, using a 25.5 Ω SPRT. The method of direct comparison is described in detail in [5].

During the freezing and melting curve measurements, an environment of inert argon gas at 101 325 Pa pressure was maintained in the cells.

The electronic measurement equipment included an ASL F18 resistance ratio bridge, operating at a frequency of 30 Hz, and 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 were made using a 25.5 Ω SPRT at low excitation currents of 1 mA and  $\sqrt{2}$  mA to allow for the 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.

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<sup>1</sup> 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.

**Enthalpy of Fusion Measurements:** Seven indium samples, 5 mg to 15 mg each, cut from a 1 g ingot of SRM 2232 and seven tin samples, 9 mg to 14 mg each, cut from a 6.25 cm<sup>2</sup> sheet of SRM 2220 were used in the DSC measurements which were performed on a Perkin Elmer DSC 7 Differential Scanning Calorimeter. The temperatures of fusion for tin and indium were used to calibrate the temperature axis. The enthalpy of fusion of tin was used to calibrate the measured energy (measured area). After linearization of the temperature axis, the temperatures and enthalpies of fusion were measured for the set of seven SRM 2220 tin samples used in the calibration of the instrument. Duplicate measurements were made on seven SRM 2232 indium samples to determine the certified values and the observed variability due to the instrument and sample configuration. A typical DSC melting curve of the indium is shown in Figure 4.

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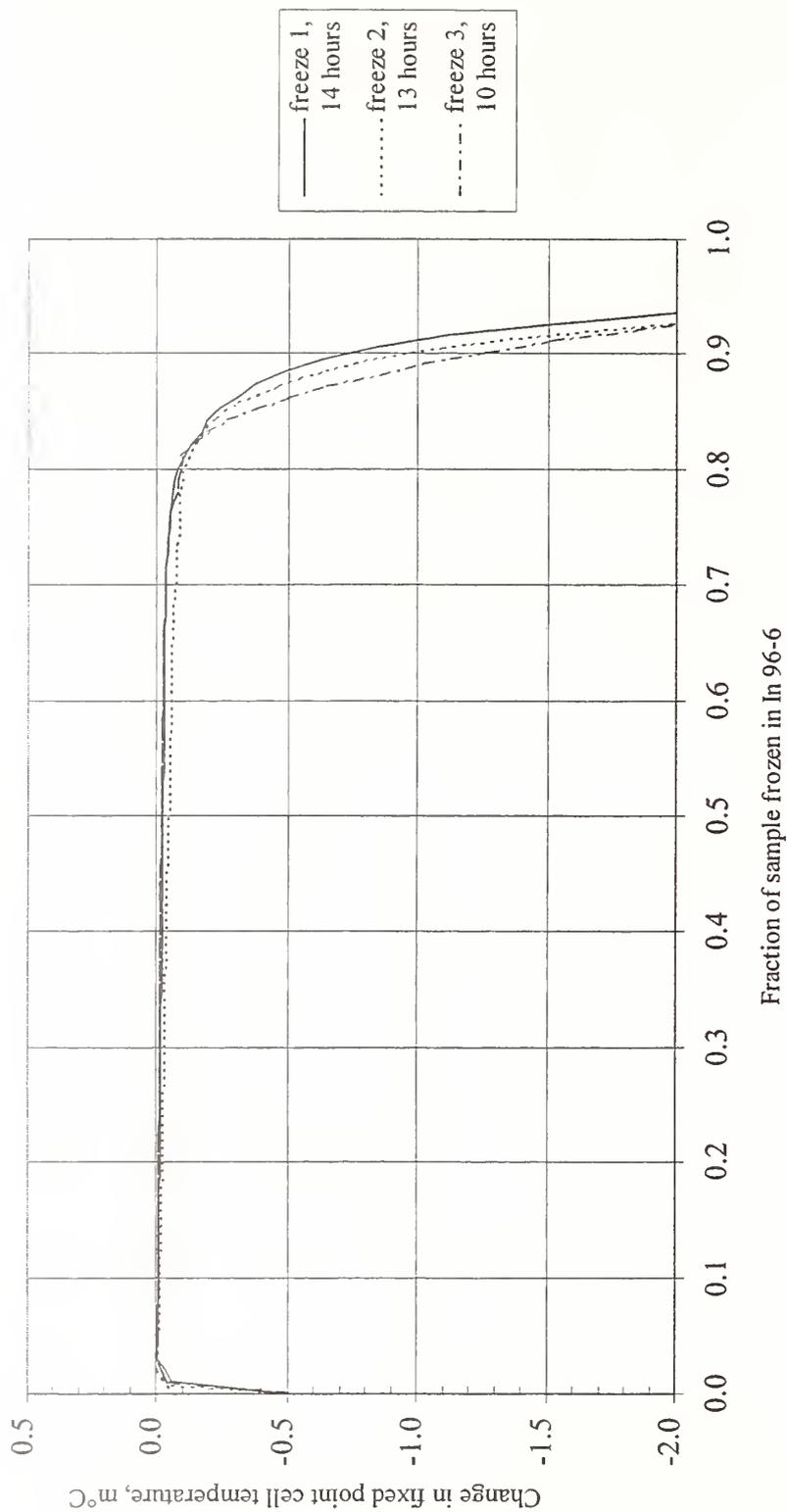


Figure 1. The freezing curves of SRM 2232 Indium DSC Calibration Standard using the "induced inner freeze" preparation technique.

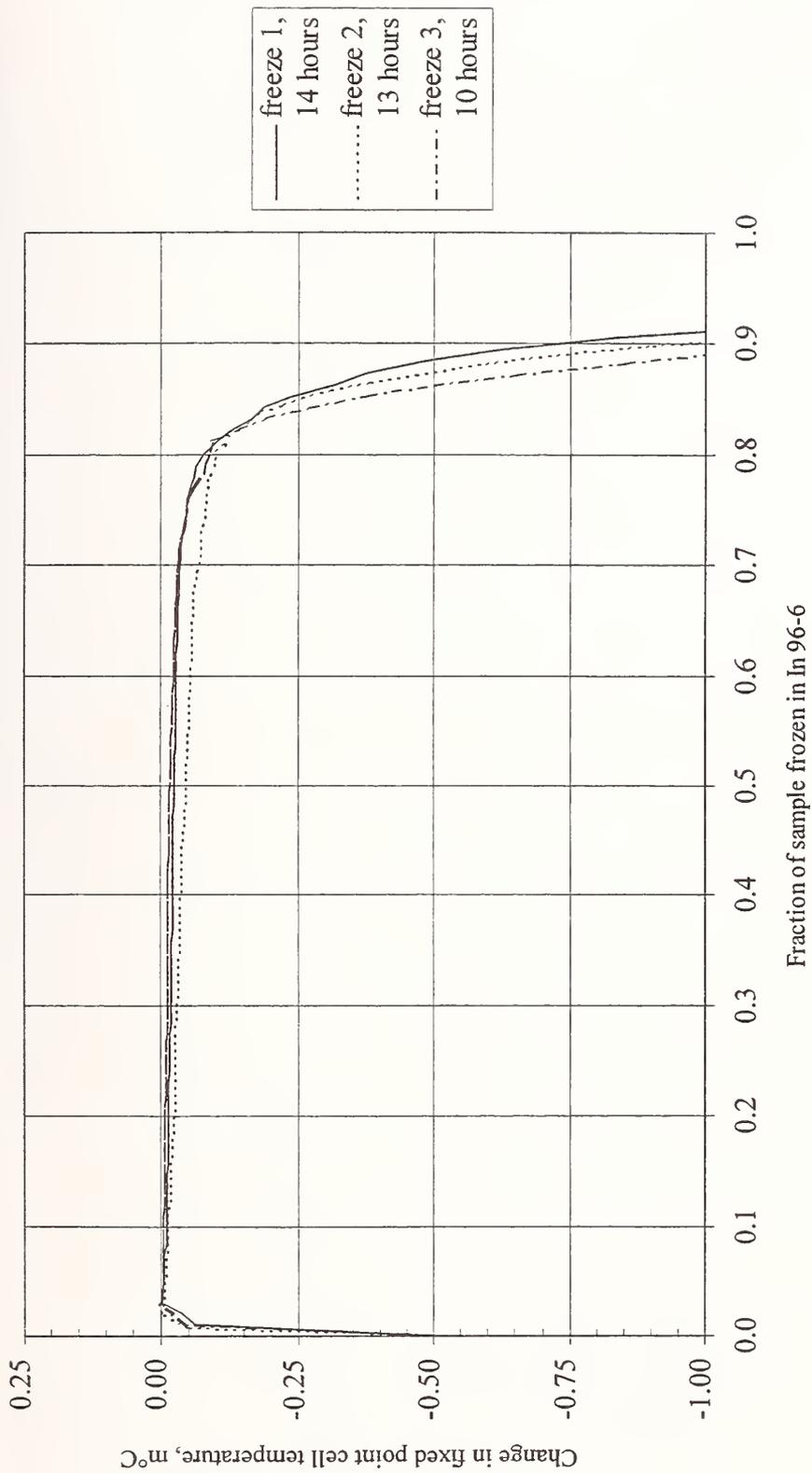


Figure 2. The freezing plateau regions of Figure 1 at greater resolution.

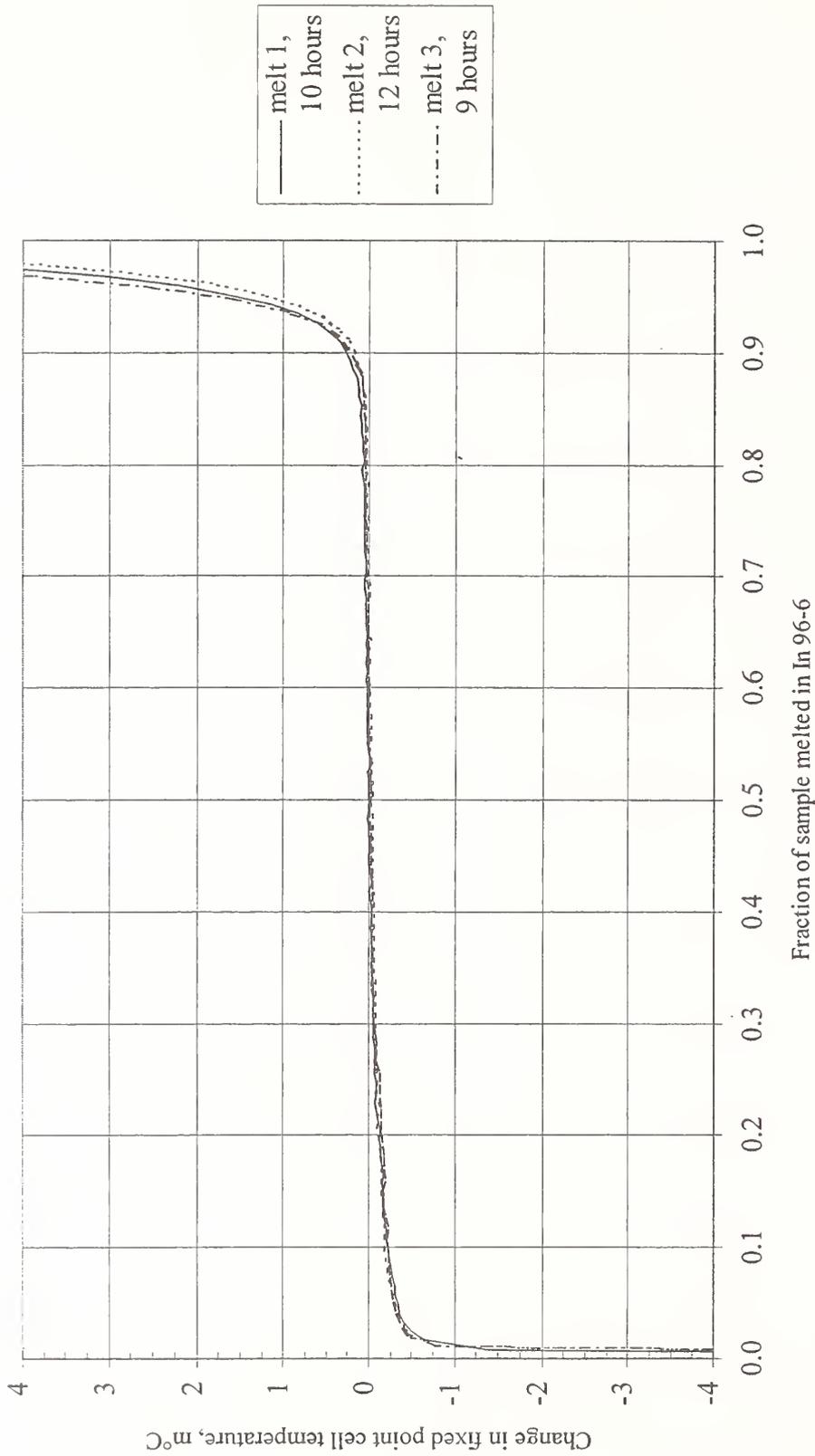


Figure 3. Three melting curves of SRM 2232 Indium DSC Calibration Standard following a slow freeze. Each melt followed the respective slow freeze of Figure 1.

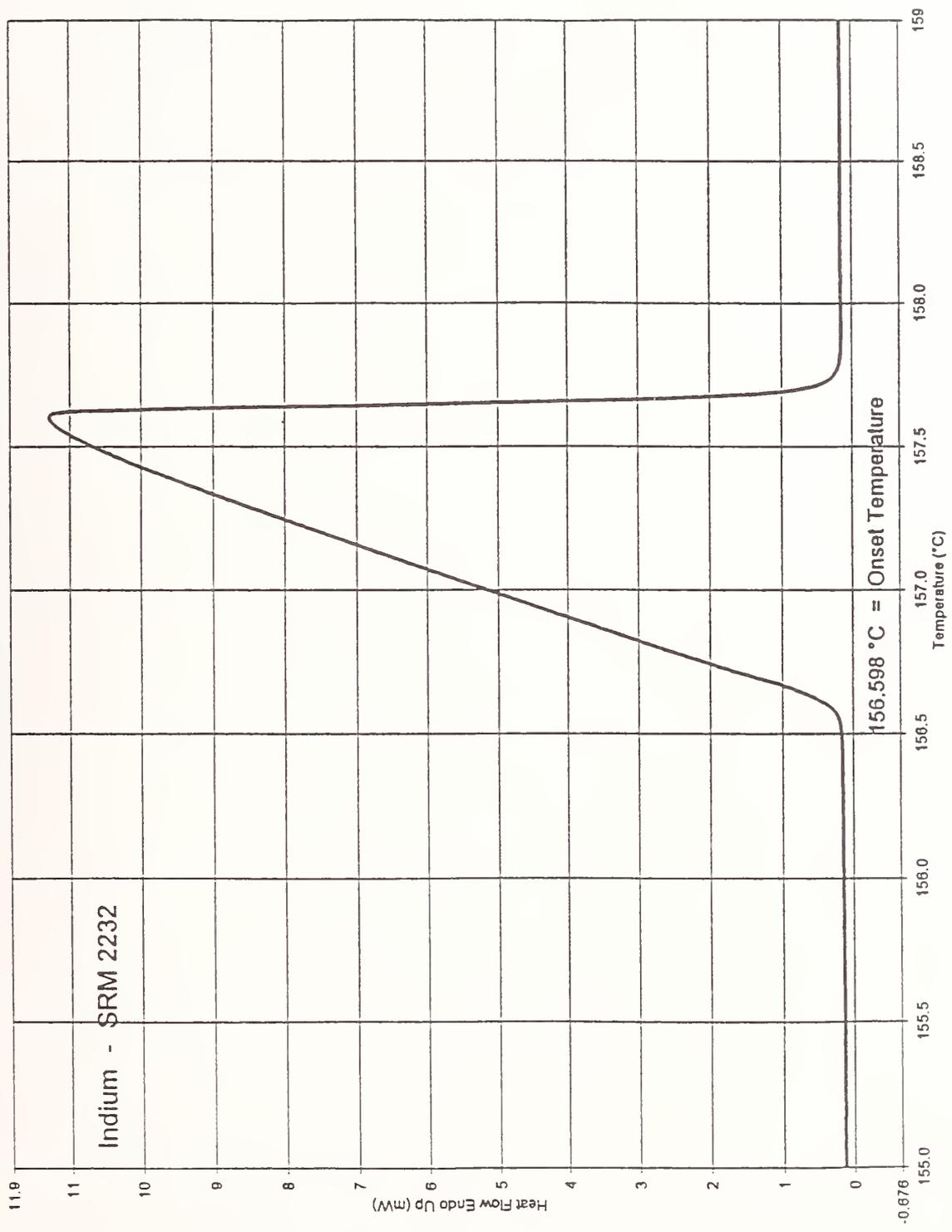


Figure 4. Typical DSC melting curve for SRM 2232 Indium DSC Calibration Standard.







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