NIST Special Publication 260-157

Standard Reference Material 1751: Gallium Melting-Point Standard

Gregory F. Strouse

NIST Special Publication 260-157

Standard Reference Material 1751: Gallium Melting-Point Standard

Gregory F. Strouse

Chemical Science and Technology Laboratory
Process Measurements Division
National Institute of Standards and Technology
Gaithersburg, MD 20899-8363

August 2004

U.S. Department of Commerce
Donald L. Evans, Secretary

Technology Administration
Phillip J. Bond, Under Secretary for Technology

National Institute of Standards and Technology
Arden L. Bement, Jr., Director

National Institute of Standards and Technology Special Publication 260-157
Natl. Inst. Stand. Technol. Spec. Publ. 260-157, NNN pages (August 2004)
CODEN: NSPUE2

U.S. GOVERNMENT PRINTING OFFICE
WASHINGTON: 2004

For sale by the Superintendent of Documents, U.S. Government Printing Office
Internet: bookstore.gpo.gov — Phone: (202) 512-1800 — Fax: (202) 512-2250
Mail: Stop SSOP, Washington, DC 20402-0001

Standard Reference Material 1751: Gallium Melting-Point Standard

Gregory F. Strouse
National Institute of Standards and Technology
Process Measurements Division
Gaithersburg, MD 20899

Abstract

The melting point of gallium (29.7646 °C) is a defining thermometric fixed point of the International Temperature Scale of 1990 (ITS-90). Realization of this melting point is performed using a fixed-point cell containing high-purity (≥99.999 99 wt. % pure) gallium. A 30 kg single lot of gallium (99.999 995_6 wt. % pure) constituting Standard Reference Material® (SRM®) 1751 was evaluated, and certified as suitable for use in the realization of the melting-point temperature of gallium for the ITS-90. Based on results obtained with three fixed-point cells containing random samples of SRM 1751, the expanded uncertainty (k=2) assigned to the melting-point temperature of the metal is 0.07 mK. In this document, the methods used for the fabrication of the gallium melting-point cells and for the evaluation of SRM 1751 are described.

Disclaimer

Acknowledgment

The author wishes to thank the Standard Reference Materials Program for their support in the development of this new SRM.

1. Introduction

One of the thermometric fixed points required to realize the International Temperature Scale of 1990 (ITS-90) is that of the gallium melting point [Ga MP (29.7646 °C)] [1]. The Ga MP is realized by using fixed-point cell containing high-purity (≥99.999 99 wt. % pure) gallium metal with an inert gas pressure of 101325 Pa. Such a fixed-point cell is used for the ITS-90 calibration of standard platinum resistance thermometers (SPRTs) over the subranges from –39 °C to 30 °C and from 0 °C to 30 °C. Additionally, the W(Ga MP) [W(Ga MP) = R(Ga MP) / R(0.01 °C), where R is resistance] provides a check on the ITS-90 criteria [W(Ga MP) ≥ 1.11807] of the purity of the Pt used in the SPRT resistor element. The Standard Reference Material® (SRM®) Ga MP Standard (SRM 1751) was developed to provide evaluated and certified material for the purpose of realizing the ITS-90 Ga MP.

The SRM 1751 certification was performed by fabricating and evaluating three fixed-point cells (designated Ga 981, Ga 982, and Ga 983) each containing random samples of the 30 kg single lot of high-purity (99.999 995$_6$ wt. % pure) metal. The certification process includes the evaluation of the sample assay, SPRT immersion characteristics, melting curves and the direct comparison with the laboratory Ga MP reference cell (Ga 944) 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 determine the melting-point temperature of SRM 1751 relative to the gallium (99.999 998 wt. % pure) used in Ga 944, and the expanded uncertainty (k=2) assigned to the melting-point temperature of SRM 1751.

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

2.1 SRM sample

The high-purity (99.999 995$_6$ wt. % pure) gallium metal that is used for SRM 1751 was purchased by the NIST Standard Reference Materials Program from Rhodia-Chimie* of France. A 30 kg single lot (lot number 9800763) of high-purity gallium metal constitutes SRM 1751. Rhodia-Chimie filled 150 plastic bottles, each containing 200 g of gallium sealed in an argon atmosphere. The purification and emission spectrographic assay of lot number 9800763 was performed by Rhodia-Chimie. The emission spectrographic assay of the gallium metal shows the total impurity level to be 0.044 μg/g, resulting from 0.001 μg/g of Al, 0.002 μg/g of Cl, 0.005 μg/g of Cu, 0.004 μg/g of Fe, 0.01 μg/g of Ni, 0.01 μg/g of Pb, 0.001 μg/g of Ti, 0.01 μg/g of Tl and 0.001 μg/g of V.

Prior to testing the fabricated Ga MP cells, the refiner sample assay is used to determine the type and concentration of each impurity in the gallium sample. From those impurity concentrations, a mole fraction sum of impurity component analysis is used to estimate the effect on the realization temperature of the Ga MP. As given in table 1, the impurity concentrations (wt %) are converted to mole fraction concentrations and summed to determine the total mole fraction impurity concentration in the fixed-point sample for the estimation of the impurity uncertainty component.

Using the total mole fraction impurity concentration contained in the Ga MP sample and the first cryoscopic constant, the impurity uncertainty component value is estimated using Raoult's Law of

Dilute Solutions [2,3]. With the distribution coefficient (k) of each impurity set at zero, such that the impurities are only soluble in the liquid sample, the equation simplifies to:

$$\Delta T = T_0 - T = \frac{x_2}{A} \qquad (1)$$

where T_0 is the freezing point temperature of the 100% pure sample, T is the observed realization temperature, x_2 is the mole-fraction impurity concentration, and A is the first cryoscopic constant of 0.00732 for gallium. The dilute amount of impurities present in the fixed-point sample are assumed to be colligative, such that the mole-fraction impurities may be summed and used with the first cryoscopic constant for the fixed-point sample in equation 1 to estimate the impurity uncertainty component value [3]. Table 1 gives the mole fraction impurity analysis for the gallium sample and the estimated impurity effect on the realized temperature of the Ga MP.

Table 1. Mole fraction impurity analysis of the Ga sample (lot number 9800763) for SRM 1751.

assay element	**impurity, wt %**	**atomic weight**	**# of AW atoms**	**mole fraction atm fraction, %**
Al	1E-09	27.0	4E-11	2.58E-09
Cl	2E-09	35.5	6E-11	3.93E-09
Cu	5E-09	63.5	8E-11	5.49E-09
Fe	4E-09	55.8	7E-11	4.99E-09
Ni	1E-08	58.7	2E-10	1.19E-08
Pb	1E-08	207.2	5E-11	3.36E-09
Ti	1E-09	47.9	2E-11	1.46E-09
Tl	1E-08	204.4	5E-11	3.41E-09
V	1E-09	50.9	2E-11	1.37E-09
Ga	0.99999996	69.7	1E-02	

Mole fraction sum of impurity concentrations	3.85E-08
1st cryoscopic constant for Ga	0.00732
Estimated impurity uncertainty component value, mK	0.01

If the table 1 value of 0.01 mK for the effect of impurities on the Ga MP realization temperature is larger than the value determined from the evaluation results from the certification of the Ga sample, then the larger value is used for the impurity effect uncertainty component. Following the analysis of the sample assay, the next step was to fabricate and evaluate three Ga fixed-point cells to certify the Ga sample for use as SRM 1751.

2.2 Gallium fixed-point cell

The three thermometric fixed-point cells (Ga 981, Ga 982, and Ga 983) were fabricated and assembled at NIST. Each cell contains 1000 g of the Ga sample from 15 randomly selected bottles (3000 g) from the 150 bottles of the 30 kg single lot.

As shown in figure 1, the borosilicate glass outer envelope, polytetrafluoroethylene (PTFE) crucible, borosilicate glass re-entrant well and valve/sealed (GTGV) gallium fixed-point cell is of the type normally used at NIST [4-7]. The borosilicate outer envelope and a single borosilicate glass piece comprised of a re-entrant well and top are fused together on completion of the cell. A borosilicate pumping tube is part of the top. The inner diameter of the re-entrant well is 8 mm with an outer diameter of 11 mm. The pumping tube with an attached valve is used to evacuate the cell to realize the triple point or fill with 101 325 Pa ±133 Pa of argon to realize the melting point. The PTFE crucible and its cap were machined from virgin PTFE. The PTFE crucible was designed with five ribs spaced 54 mm apart to provide structural integrity to the crucible during the 3.1% expansion on solidification of the gallium and to minimize thermal contact with the outer borosilicate-glass envelope. Similarly, the PTFE crucible rests on a Nylon ring inside the outer borosilicate-glass envelope to thermally isolate the bottom of the crucible from the outer borosilicate-glass envelope. The borosilicate-glass re-entrant well passes through the PTFE cap in the top of the PTFE crucible. The immersion depth for the cells from the bottom of the glass re-entrant well to the top of the metal surface is 20.5 cm.

Figure 1a.

Figure 1b.

Figure 1c.

Figure 1. a) borosilicate glass re-entrant well and valve/sealed (GTGV) gallium fixed-point cell, b) fused glass envelope and reentrant well with pumping tube and attached valve c) Nylon thermal isolation ring.

2.3 Assembling of the fixed-point cell

Any handling procedure of high-purity material is apt to introduce contamination. The small, argon-filled plastic bottles are convenient for handling and filling during melting-point cell construction. In order to maintain the purity of the gallium, one-time use, powder-free surgical gloves were used when handling any components that come in contact with the gallium during the cleaning and fabrication processes.

Prior to filling the PTFE crucible, the crucible was cleaned to remove any contaminants from the machining process. The cleaning process was (1) clean in hot, soapy water; (2) rinse with copious amounts of water; (3) soak in 20% nitric acid-80% distilled water (volume) for 1 hour; (4) rinse with copious amounts of distilled water, and then (5) air dried. In addition, the borosilicate glass and Nylon parts were cleaned using the same process given above.

After all of the fixed-point cell parts were cleaned, the parts and the bottles containing the Ga were placed and sealed in the argon-filled glove box. Prior to melting the Ga and assembling the fixed-point cell, dried argon gas was used to overpressure the glove box such that a constant flow of argon was used to purge the glove box for two days. In order to introduce 1000 g of Ga into the crucible and insert the borosilicate re-entrant well, the Ar-filled glove box environment was heated to 40 °C overnight to melt the Ga. The order of assembly was as follows: (1) the Nylon ring was placed in the bottom of the borosilicate glass envelope, (2) the bottom of PTFE crucible was centered on the Nylon ring, (3) the gallium was poured into the PTFE crucible, (4) the PTFE cap was screwed into the top of the PTFE crucible, (5) the borosilicate reentrant well was inserted through the PTFE cap, (6) a small cleaned Nylon weight was place on the top of the reetrant well to prevent the well from floating out of position, (7) the gallium metal is solidified, (8) the solidified Ga fixed-point cell is removed from the glove box so that the glass blower can fuse the two borosilicate pieces, and then (9) a PTFE valve is place on the borosilicate pumping tube.

Care must be taken that the borosilicate envelope is properly supported and vertical so that the liquid gallium does not spill out of the PTFE crucible during the assembly process.

3. Certification Procedure for SRM 1751

The steps involved in certifying the Ga MP sample for use as SRM 1751 involves the several experimental evaluation steps of the three assembled Ga fixed-point cells. The first step is to obtain heat flux (immersion) characteristics of a 25.5 Ω standard platinum resistance thermometer (SPRT) to validate that SPRT is in near thermal equilibrium with phase transition of the Ga. The second step is to obtain three melting curves for estimating the impurity of the Ga sample contained within the three Ga MP cells. The third step is to directly compare the realization temperature of the three Ga MP with that of the NIST laboratory reference Ga MP cell. From the results of the three experimental evaluation steps and the calculated mole fraction impurity analysis, an uncertainty is assigned to the SRM 1751 Ga MP realization temperature.

Prior to the evaluation measurements, each Ga MP cell was attached to an oil-free diaphragm and turbo-molecular pumping system and an Ar gas handling system. The Ga MP cell was evacuated to a base pressure of at least 5×10^{-6} bar and backfilled with dry Ar to a pressure of 101325 Pa three times prior to a final evacuation and backfill of Ar. During the first realization of the Ga MP, the cell is sealed with the attached valve to a pressure of 101 325 Pa ±133 Pa. The pressure effect on the realized temperature of the Ga MP is –2.011 mK/101 325 Pa [4]. The uncertainty (k=1) in the pressure in the cell is equivalent to 0.003 mK in the realization of the Ga MP.

3.1 Measurement equipment

The instrumentation used for the measuring the cells included a commercially-available 9.5 digit ac resistance ratio bridge operating at a frequency of 30 Hz, a thermostatically-controlled (25 °C ±0.01 °C) ac/dc reference resistor and a 25.5 Ω SPRT. A detailed description of the measurement system is found in reference [8,9]. SPRT measurements of the melting-point plateaus were made with an excitation current of 1.0 mA. SPRT measurements of the heat flux (immersion) characteristics and the direct comparisons were made with two excitation currents of 1.0 mA and 1.414 mA for extrapolation to 0 mA. The 1 mA reading was repeated after the 1.414 mA reading to insure that the SPRT was at thermal equilibrium. The two 1 mA readings were required to repeat to within the equivalent of ±0.01 mK for the measurements to be valid. Following each experimental measurement set at the Ga MP, the SPRT was measured at the triple point of water [TPW, (0.01 °C)].

Three furnaces are used for realizing the Ga MP. Each of the furnaces consists of a closed-bottom cylindrical-tube aluminum core with a non-inductively, single-layer, bifilarly wound heater on the outside of the core. The furnaces are designed to provide about a 1 mm annular space between the Ga cell and the inner wall of the aluminum core. The aluminum core is filled with mineral oil to improve thermal contact between the cell and the furnace core. One of the three furnaces which operates at 40 °C ±0.01 °C is used for the preparation of the outer liquid-solid interface. In this furnace, the melting-point plateau will last approximately 13 hours. The other two furnaces operate at a temperature of 30 °C ±0.01 °C. In these two furnaces, the melting-point plateau will last at least one month. An immersion heater operating at a temperature of 40 °C is used to establish the inner liquid-solid interface. During preparation of the melting-point plateau and during subsequent measurements, the thermometer well is completely filled with mineral oil to improve thermal contact of the immersion heater and of the SPRT, and to improve the heat flux (immersion) characteristics of the SPRT.

3.2 Melting-point realization method

In the realization of the Ga MP, the recommended “induced inner melt” method [4-6] was used. The inner liquid-solid interface around the borosilicate reentrant well is the realization (phase-transition) temperature that SPRT senses and the outer liquid-solid interface around the inside of the crucible outer wall provides a buffer for the small fluctuations in the maintenance furnace.

Prior to realizing the Ga MP, the gallium sample is solidified by placing the cell in a glass beaker that extends over the length of the cell. The beaker was filled 1/3 of the way with crushed dry ice; after 20 minutes 2/3 of the way with crushed dry ice; and after another 20 min all of the way with crushed dry ice. In approximately three hours, the gallium in the cell was frozen. Since the gallium metal expands 3.1 % on solidification, it is important to freeze the gallium from the bottom to the top of the crucible to prevent breakage of the cell. Since the gallium is ≥99.999 99 wt. % pure, the observed effect on the realized melting-point temperature from using any of the three methods for solidifying the gallium sample (freezing from the outside inward, freezing from the inside outward, and from the inside and outside) does not differ by no more than the reproducibility of measurement system of 0.01 mK [6]. As described, the first method (freezing from the outside inward) is the technique normally used at NIST to solidify the gallium prior to realization of the melting point.

Two liquid-solid interfaces are created in order to achieve the Ga MP. The fixed-point cell is placed in the 40 °C furnace to establish the outer liquid-solid interface and an immersion heater (operating at 40 °C) is placed into the re-entrant well for 45 min to establish a complete inner liquid-solid interface. For the melting curve evaluations, the Ga MP cell is left in the 40 °C furnace and for the heat flux (immersion) and direct comparison evaluations, the Ga MP cell is placed in the 30 °C furnace during the measurements, respectively.

3.3 Heat flux (immersion) characteristics

Proper immersion of the SPRT in each fixed-point cell was verified by determining if the SPRT could track the assigned hydrostatic-head effect of Ga (–1.2 mK/m) during the Ga MP realization [1]. The SPRT must be able to track the hydrostatic-head effect over at least the bottommost 3 cm of the reentrant well to ensure that the thermometer is in near-thermal equilibrium with the phase-transition temperature of the Ga MP [10].

The determination of the heat flux (immersion) characteristics is determined by measuring the SPRT starting 10 cm from the bottom of the thermometer well, then inserting the SPRT in 2 cm steps until 4 cm from the bottom, at which time the SPRT was then inserted in 1 cm steps until the bottom of the thermometer well was reached. Before measuring the SPRT at each step, twenty minutes were allowed for the SPRT to re-equilibrate after changing the immersion depth. The immersion depth of the SPRT was calculated from the sensor midpoint to the height of the metal column during the melting-point realization with approximately 20 % of the metal melted. Approximately 6 h is required to complete the heat flux measurements. As shown in Figure 2, the SPRT (coiled-helix sensor) is capable of tracking the hydrostatic-head effect of the Ga MP in the SRM cells over the bottommost 8 cm. From these measurements, a heat flux uncertainty (k=1) is calculated as the difference at 3 cm from the bottom of the reentrant well between the value as calculated from the linear fit of the measurements over the bottommost 5 cm and the ITS-90 assigned gallium hydrostatic-head effect.

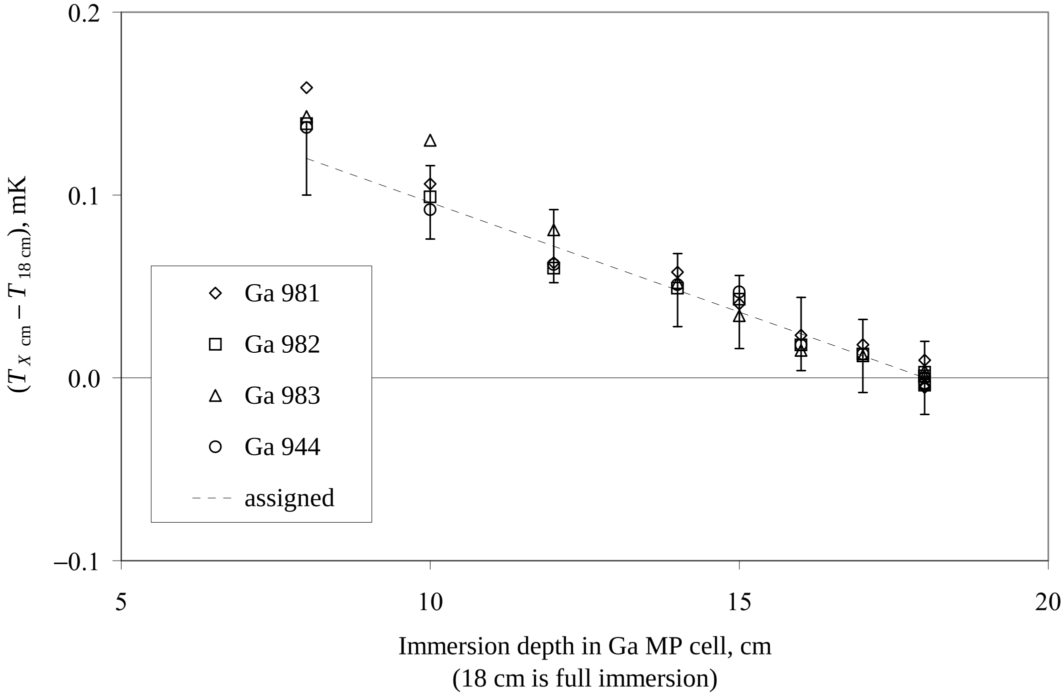

Figure 2. Heat flux immersion profile test of the SPRT during the realization of the Ga MP in the three SRM 1751 cells (Ga 981, Ga 982, and Ga 983) and the NIST laboratory reference cell (Ga 944) with respect to the assigned value of the hydrostatic-head effect.

It is important to note that there is a strong interaction between the fixed-point cell, maintenance system, and the SPRT during the realization of the fixed point. Different designs of the fixed-point cell, maintenance system, or SPRT may change the heat flux (immersion) characteristics and will require re-determination of the heat flux uncertainty. For the heat flux measurements, it is useful for the realization curve to last at least 30 h, so that the measurements are made over the first 20 % of the realization. Additionally, the method used to realize the Ga MP impacts the SPRT heat flux (immersion) characteristics and measured phase-transition temperature [6].

3.4 Melting-point realization curves

Using an excitation current of 1 mA, thermometer readings were recorded continuously until the melting was complete (SPRT registers 10 mK above the plateau temperature). After each melting-point realization, the SPRT was measured at the TPW to ensure that the thermometer had not changed.

Figures 3 through 6 show the melting curves for each of the three Ga MP cells (Ga 981, Ga 982, Ga 983) and for comparison purposes the reference Ga MP cell (Ga 944), respectively. Using an excitation current of 1 mA, thermometer readings were recorded continuously until the melting was complete (10 mK above plateau). The average length of a melting curve was 13 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 mK point on the graph. The melting plateau range (0 % to 100 % melted) is calculated using the linear fit of the realization plateau in the 10 % to 90 % melted range. From the graphs, the average temperature ranges of the melting plateaus were 0.00 mK, 0.00 mK, 0.00 mK, and 0.00 mK, for Ga 981, Ga 982, Ga 983, and Ga 944, respectively.

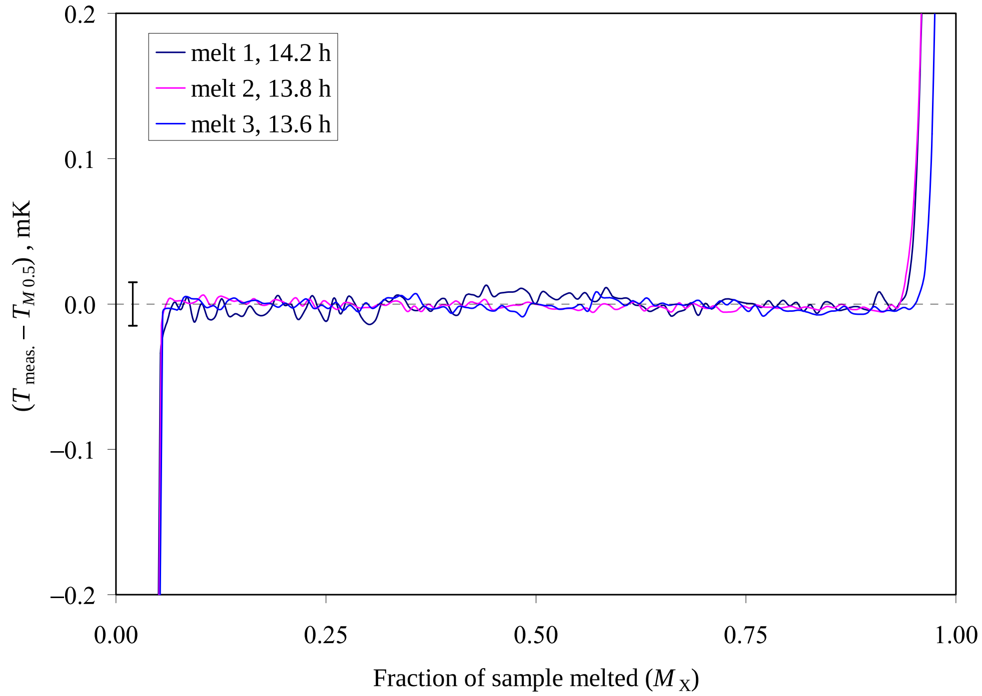

Figure 3. Melting curves for Ga 981. The uncertainty bar (k=2) represents the repeatability of the measurement system during the Ga MP realization ($M_{0.1}$ to $M_{0.9}$).

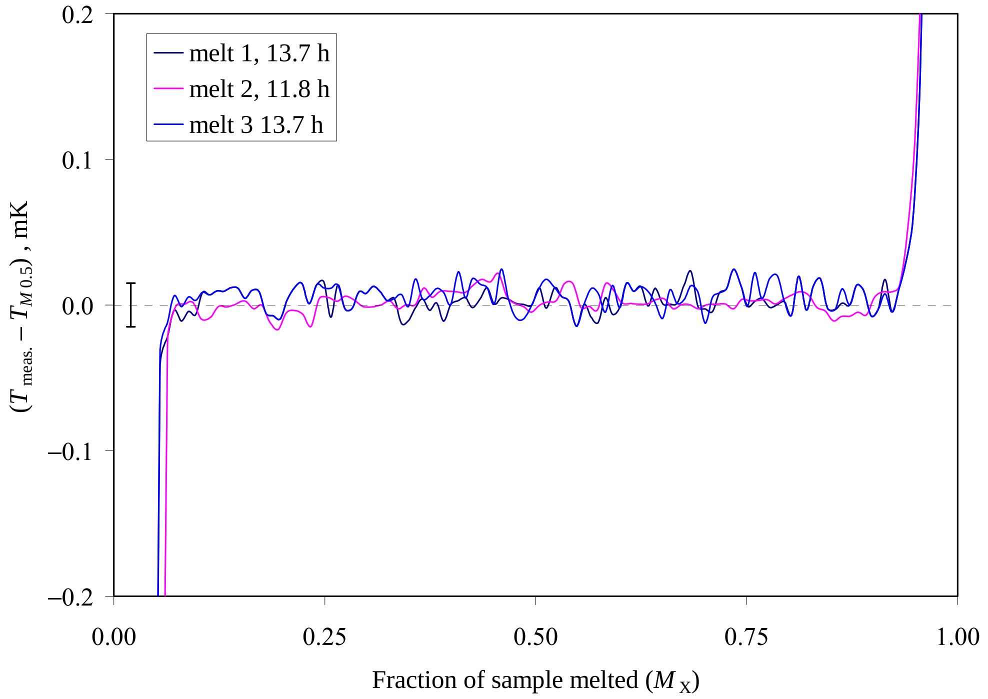

Figure 4. Melting curves for Ga 982. The uncertainty bar (k=2) represents the repeatability of the measurement system during the Ga MP realization ($M_{0.1}$ to $M_{0.9}$).

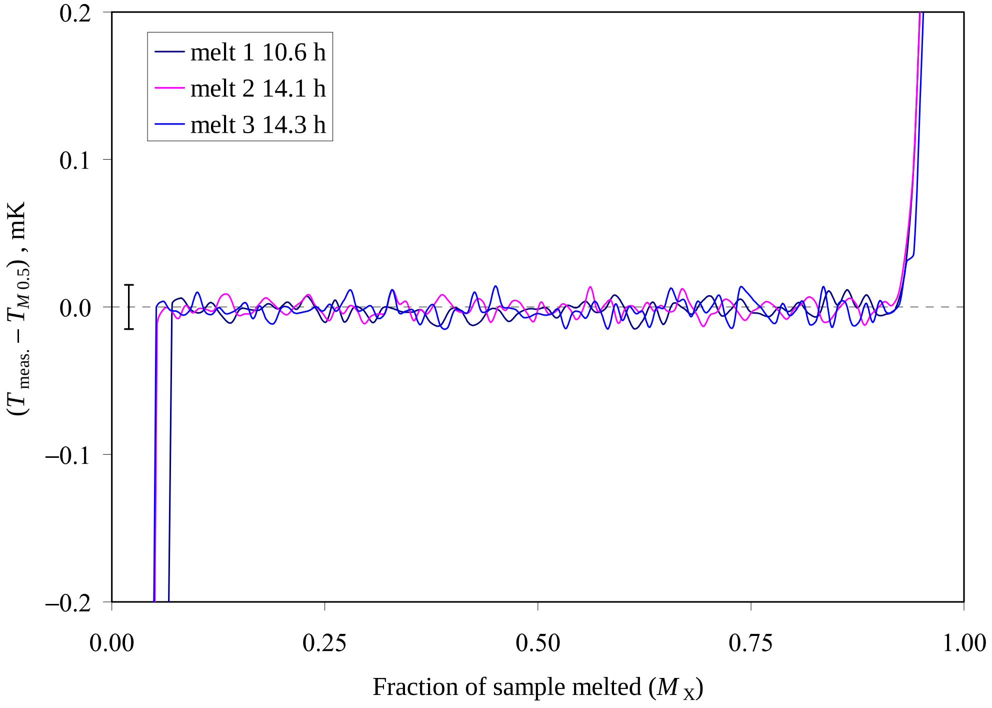

Figure 5. Melting curves for Ga 983. The uncertainty bar (k=2) represents the repeatability of the measurement system during the Ga MP realization ($M_{0.1}$ to $M_{0.9}$).

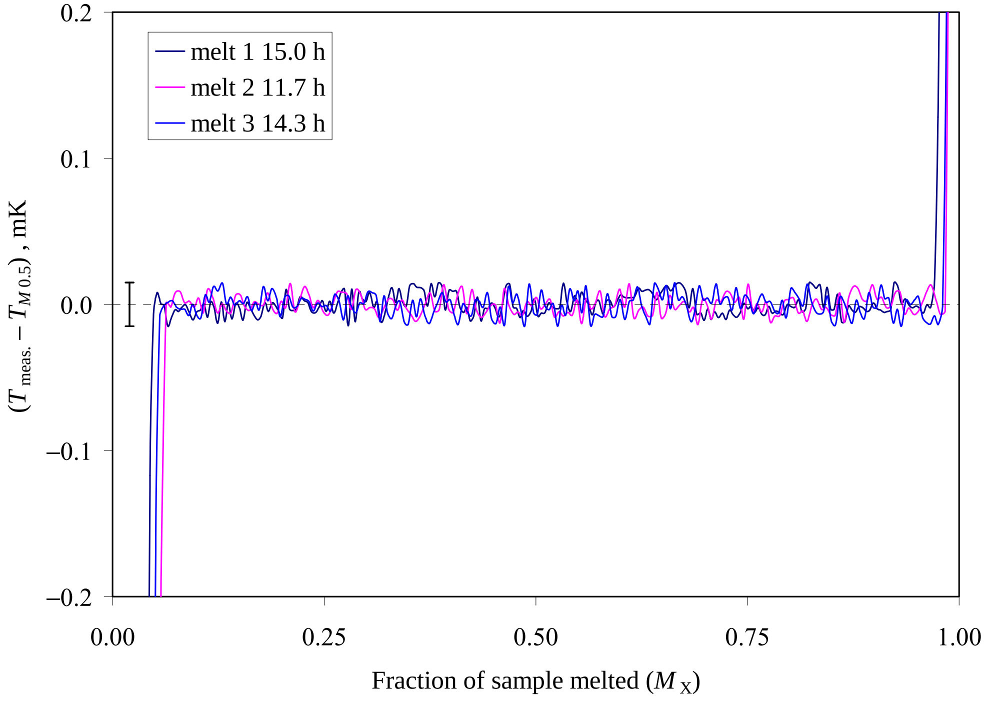

Figure 6. Melting curves for Ga 944. The uncertainty bar (k=2) represents the repeatability of the measurement system during the Ga MP realization ($M_{0.1}$ to $M_{0.9}$).

Since a freezing curve is difficult to obtain for Ga, the melting curve may be plotted as ΔT as a function of the reciprocal fraction melted ($1/M_X$) for estimating the mole fraction impurity concentration in the fixed-point sample. A linear regression from a $1/M_X$ value of 1.5 (denoted $1/M_{1.5}$) to $1/M_5$ is used to determine the slope of the $1/M$ plot. Using Raoult's Law of dilute solutions [2,3], the $\Delta T(1/M_1 - 1/M_0)$ value for the fit is used as the experimental estimation of the mole fraction impurity concentration in the fixed-point sample. The equation is written as:

$$x_2 = \Delta T(1/M_1 - 1/M_0)\,A$$

where x_2 is the overall mole fraction impurity concentration, and A is the first cryoscopic constant.

Figures 7 through 10 show the melting curves plotted as ΔT as a function of the reciprocal fraction melted ($1/M_X$) for the three Ga MP cells (Ga 981, Ga 982, and Ga 983) and for comparison purposes the NIST reference Ga MP cell (Ga 944), respectively.

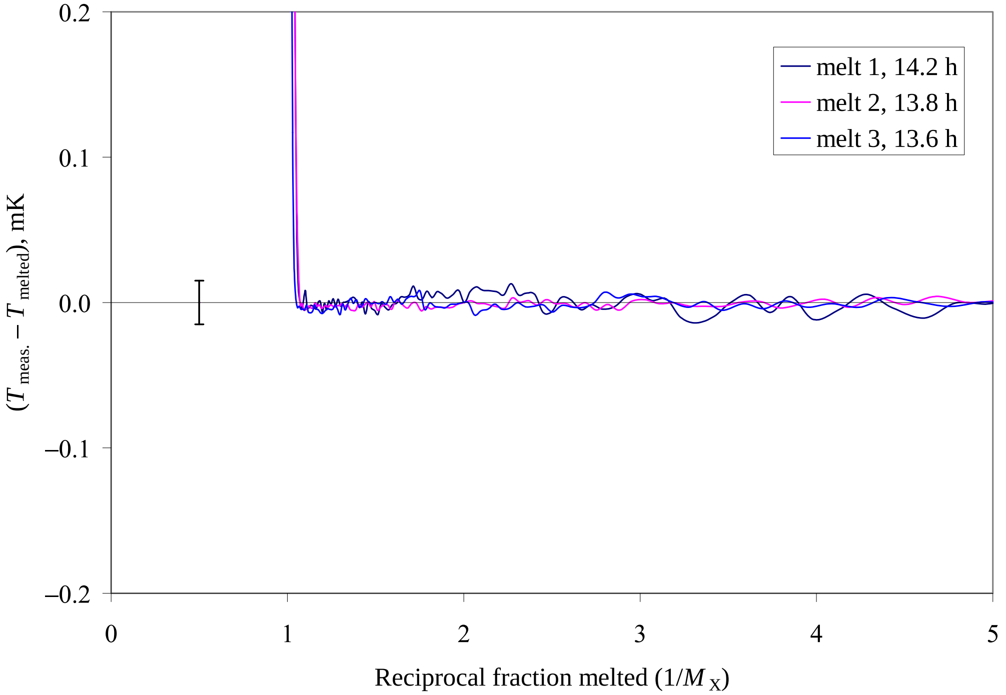

Figure 7. Reciprocal fraction melted (1/M_X) curves for Ga 981. The uncertainty bar (k=2) represents the repeatability of the measurement system during the Ga MP realization ($M_{0.1}$ to $M_{0.9}$).

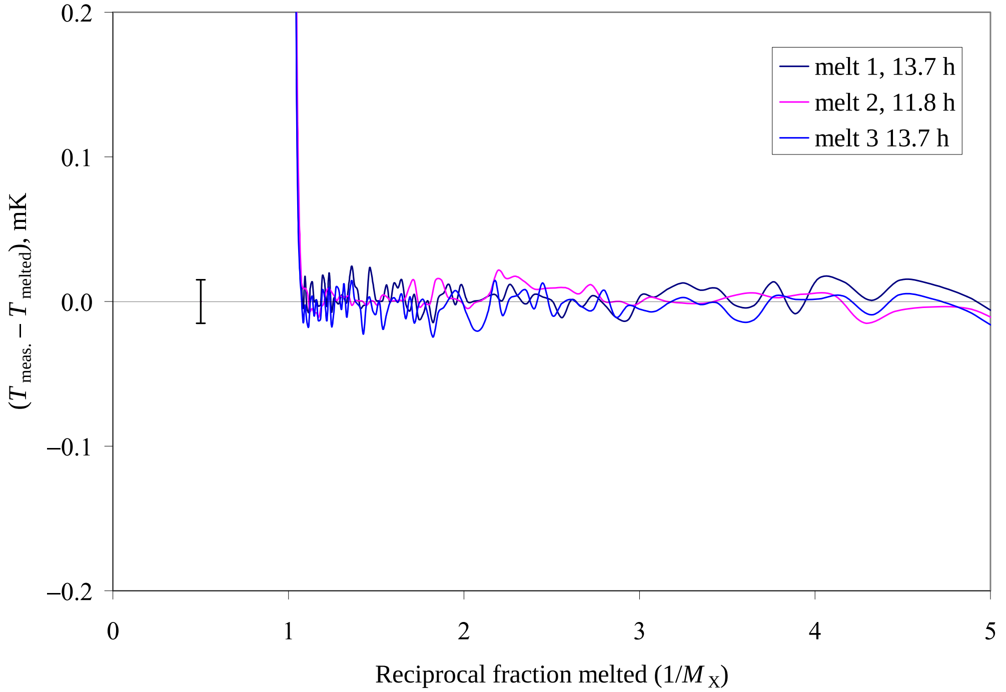

Figure 8. Reciprocal fraction melted (1/M_X) curves for Ga 982. The uncertainty bar (k=2) represents the repeatability of the measurement system during the Ga MP realization ($M_{0.1}$ to $M_{0.9}$).

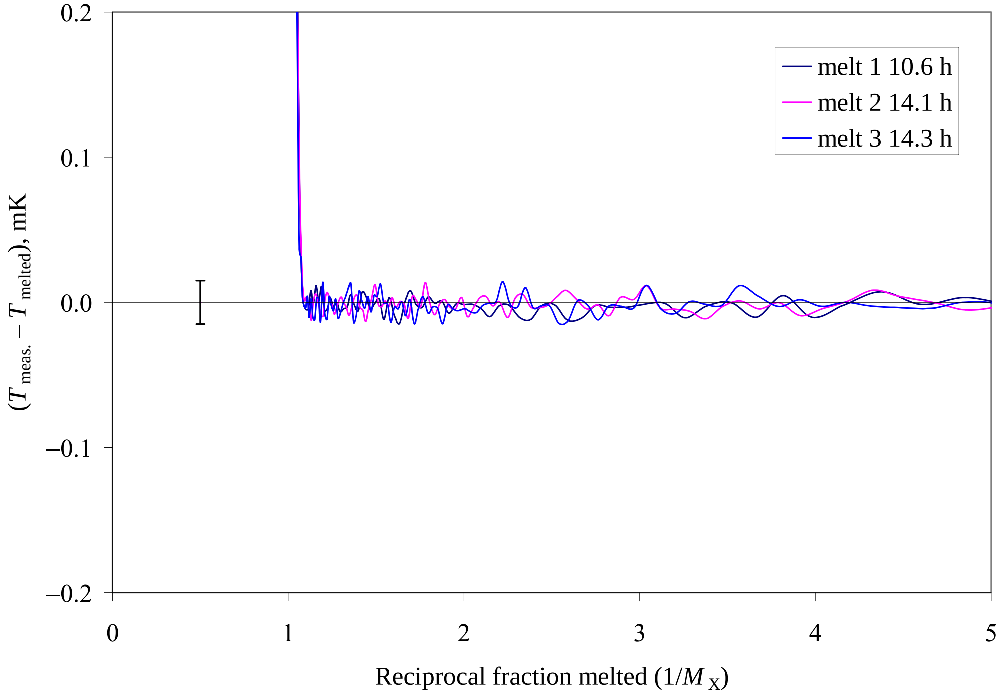

Figure 9. Reciprocal fraction melted (1/M_X) curves for Ga 983. The uncertainty bar (k=2) represents the repeatability of the measurement system during the Ga MP realization ($M_{0.1}$ to $M_{0.9}$).

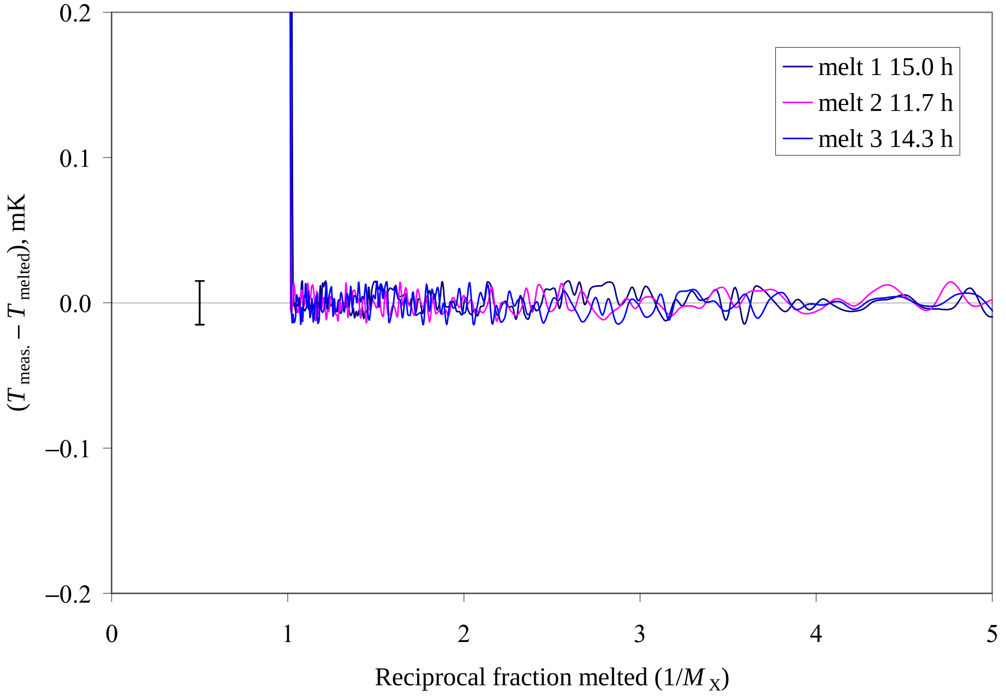

Figure 10. Reciprocal fraction melted (1/M_X) curves for Ga 944. The uncertainty bar (k=2) represents the repeatability of the measurement system during the Ga MP realization ($M_{0.1}$ to $M_{0.9}$).

Table 2 compares estimated impurity concentration for the SRM 1751 gallium as calculated using the mole fraction sum of impurity concentration method (Table 1) with the $1/M_X$ melting-curve method. The results of the two methods indicate that the SRM gallium is of similar purity to that used for the NIST laboratory reference Ga MP cell.

Table 2. Estimated impurity concentration results of the mole fraction sum of impurity method and the $1/M_X$ melting-curve method.

Ga MP cell	Mole fraction sum of impurity concentration, x 10^9	$1/M_X$ estimated impurity concentration, x 10^9
Ga 944 (reference)	47.2	7.1
Ga 981	38.5	8.6
Ga 982	38.5	9.9
Ga 983	38.5	4.8

Since the $1/M_X$ realization curve method gives a smaller value than that of the mole fraction sum of impurity components method, the mole fraction sum of impurity components method is used to estimate the impurity uncertainty component value of the fixed-point cell. Additionally, This crosscheck analysis ensures that no further impurities were added to the gallium sample during the fabrication of the fixed-point cells.

A smaller value from the $1/M_X$ realization curve method may mean that the refiner sample assay over-estimated the amount of impurities or the distribution coefficients of one or more of the impurities approaches one. An impurity with a distribution coefficient of one will not affect the slope of the realization curve, but will affect the realization temperature of the fixed-point cell. It is important to note that there is a limitation in using the $1/M_X$ realization curve method to estimate the purity of the metal, because the slope of a melting curve will depend upon the history of the previous freezing of the sample in the fixed-point cell. For Ga, a fast freeze (<30 min) creates a homogenous mixture of the impurities within the fixed-point sample, which in turn causes a small melting range (slope of melting curve approaches zero) and a smaller calculated impurity concentration value.

3.5 Direct comparison measurements

The direct comparison measurements are used to determine the relative realization temperature difference between the three Ga MP cells containing the SRM gallium sample and the NIST laboratory reference Ga MP cell (Ga 944). The direct comparison measurements are obtained by realizing simultaneous melts for the two cells in two separate but nearly identical furnaces and making three sets of alternate measurements, at equal time intervals, on their melting-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. The fraction of metal melted during a set of three measurements of the melting-point temperature of each cell did not exceed 20%.

Corrections were made for any differences in pressure and hydrostatic head effects in each cell. Each test Ga MP cell and the NIST reference Ga MP cell were measured using an SPRT three times during the direct comparison and this procedure was repeated two times for a total of nine measurement pairs. Following each set of direct comparison measurements, the SPRT was measured at the TPW to ensure that the thermometer had not changed.

Since the Ga MP cells are tested in nearly identical realization conditions, the realized temperature difference is a function of the purity difference between the SRM Ga sample and the NIST reference Ga sample. As shown in figure 11, the direct comparison results show that the average realized melting-point temperature difference between the Ga 981, Ga 982, and Ga 983 MP cells and the laboratory reference cell Ga 944 was 0.01 mK, –0.01 mK and 0.00 mK, respectively.

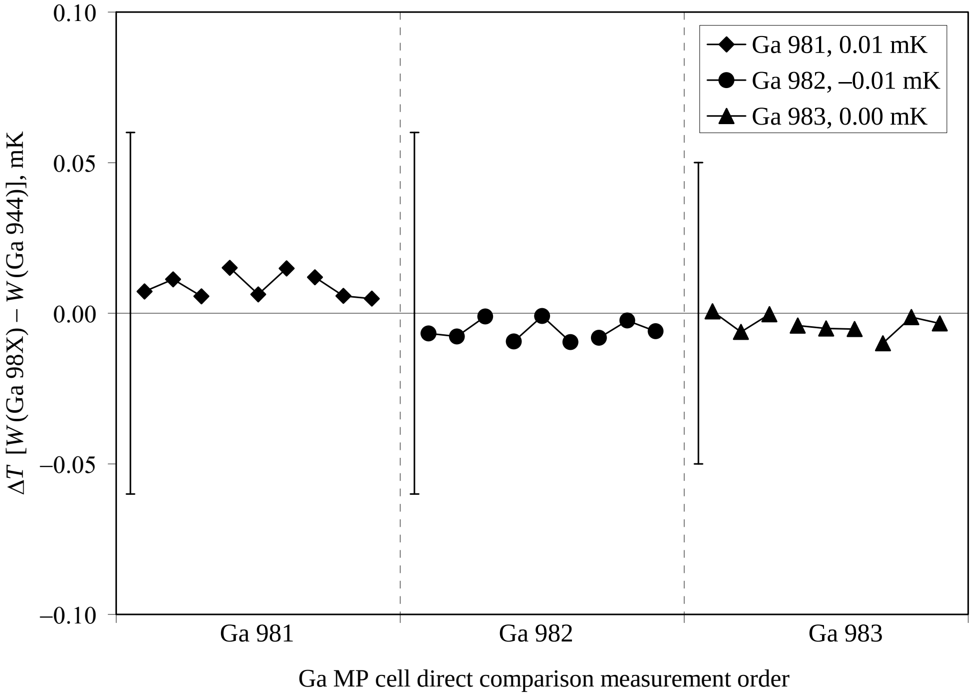

Figure 11. Direct comparison results for the Ga 981, Ga 982, and Ga 983 MP cells with respect to the NIST Ga MP reference cell Ga 944. The uncertainty bars (k=2) represent the direct comparison uncertainty for each cell.

4. Uncertainties

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

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

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 [11,12].

4.1 Uncertainty of direct comparison measurements

Many of the systematic effects that normally occur during the realization of a fixed-point cell cancel when directly comparing two fixed-point cells. There are two possible known contributions to the Type A standard uncertainty; first from the repeatability of the measurement equipment (bridge repeatability) and the second from the repeatability of both the SPRT and realization temperature of the fixed-point cell (direct comparison repeatability). There are four known contributions to the Type B standard uncertainty in the direct comparison measurements; first from the uncertainty in the exact immersion depth of the SPRT (hydrostatic head) due to the uncertainty in the position of the thermometer sensor and the uncertainty in the exact fraction of the metal sample frozen, second the SPRT self heating, third the uncertainty in the adequacy of immersion of the thermometer to eliminate the thermometer stem conduction [heat flux (immersion)] and fourth the gas pressure in the fixed-point cell.

Table 3 gives the estimation of uncertainties for the direct comparison measurements. The expanded uncertainty (*k*=2) in the direct comparison measurements of the gallium fixed-point cells containing the SRM metal is estimated to be 0.05 mK.

Table 3. Direct comparison uncertainties for the three SRM Ga MP cells.

Type A	u_i / mK			
	Ga981	**Ga982**	**Ga983**	
Bridge Repeatability	0.008	0.008	0.008	both cells
Direct Comparison Repeatibility	0.004	0.003	0.003	pooled s.d. of pair differences
Total A	0.01	0.01	0.01	
Type B (rectangular distribution unless otherwise noted)				
Hydrostatic-head	0.01	0.01	0.01	both cells
SPRT self-heating	0.02	0.02	0.02	both cells
Immersion (Heat Flux)	0.002	0.002	0.001	both cells, normal distribution
Gas pressure	0.00	0.00	0.00	both cells
Total B	0.03	0.03	0.03	
Total Standard Uncertainty (*k* =1)	0.03	0.03	0.03	
Total Expanded Uncertainty (*k* =2)	**0.05**	**0.05**	**0.05**	

4.2 Uncertainty assigned to SRM 1751

The Type A, Type B, and expanded uncertainties (*k*=2) assigned to each of the Ga MP cells containing the SRM metal is given in Table 4. The uncertainty budget is the same as that used by the NIST PRT Laboratory in assigning uncertainties to ITS-90 realization of thermometric fixed-point cells. The expanded uncertainty assigned to the SRM 1751 sample is the average of the three expanded uncertainties assigned to the Ga MP cells of 0.07 mK.

From the direct comparison measurements, the realized temperature difference between the three Ga MP cells (Ga 981, Ga 982, and Ga 983) and the NIST laboratory reference cell (Ga 944) does not exceed ±0.01 mK and is within the uncertainty of 0.01 mK assigned to the chemical impurity effect uncertainty for the SRM 1751 sample given in table 1. Thus, only the chemical impurity uncertainty value and not the differences between the three Ga MP cells and Ga 944 is used in the SRM 1751 uncertainty budget.

Table 4. Uncertainty budget for the three Ga MP cells containing the Ga SRM 1751 sample.

		u_i / mK	
	Ga981	**Ga982**	**Ga983**
Bridge Repeatability (A)	0.002	0.002	0.002
Bridge Non-Linearity (A)	0.02	0.02	0.02
Phase Transistion Realization Repeatability (A)	0.004	0.003	0.003
Direct Comparison Measurements ($\mathrm{B}_{\mathrm{rectangular}}$)	0.02	0.02	0.02
AC Bridge Quadrature Effects ($\mathrm{B}_{\mathrm{rectangular}}$)	0.01	0.01	0.01
Reference Resistor Resistance ($\mathrm{B}_{\mathrm{rectangular}}$)	0.01	0.01	0.01
Chemical Impurities ($\mathrm{B}_{\mathrm{normal}}$)	0.01	0.01	0.01
Hydrostatic Head Correction ($\mathrm{B}_{\mathrm{normal}}$)	0.00	0.00	0.00
SPRT Self-Heating Correction ($\mathrm{B}_{\mathrm{rectangular}}$)	0.01	0.01	0.01
Heat Flux ($\mathrm{B}_{\mathrm{normal}}$)	0.00	0.00	0.00
Gas Pressure ($\mathrm{B}_{\mathrm{rectangular}}$)	0.00	0.00	0.00
Slope of Plateau ($\mathrm{B}_{\mathrm{normal}}$)	0.00	0.00	0.00
Isotopic Variation ($\mathrm{B}_{\mathrm{normal}}$)	0.00	0.00	0.00
Propagation of TPW ($\mathrm{B}_{\mathrm{rectangular}}$)	0.02	0.02	0.02
u_c / mK	0.037	0.037	0.037
U (k=2) / mK	**0.07**	**0.07**	**0.07**

5. Application

In assigning a temperature value to realizations of the Ga MP, corrections must be applied for the depth of immersion of the thermometer sensing element below the surface of the metal (–1.2 mK/m) [1]. Also, if the pressure over the cell during the measurements is not controlled at 101 325 Pa, a correction (–2.011 mK/101 325 Pa) must be made for the difference in pressure [4].

For those constructing their own ITS-90 defining Ga MP cell containing SRM 1751, it is necessary to confirm that the purity of the metal was maintained during construction of that cell. Comparing the melting curves of that new cell with those shown in figures 3-5 and figures 7-9 makes this confirmation. As a continuing check on the overall purity of the gallium metal contained in the fixed-point cell, a check SPRT should be used for every realization and melting curves should be obtained once per year and compared with those obtained previously.

6. Conclusions

For the metal to be certified as a melting-point standard, the realized temperature difference between the SRM fixed-point cells and the reference fixed-point cell must be consistent with different impurity concentrations of the two samples 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 reference cell. A fixed-point cell that is "hotter" usually contains fewer impurities, since impurities in these samples will usually decrease the realized temperature. The realized temperature difference between two, properly realized, fixed-point cells is correlated to the difference in the sample impurities in each cell [3].

The evaluation of SRM 1751 for use as a Ga MP standard shows that the material is of high-purity (≥99.999 99%) and is acceptable for use as a defining fixed point of the ITS-90 and is so certified. Based on the results from the evaluation of the three fixed-point cells containing the SRM metal, the average temperature change of the melting-point plateau (10% to 90% melted) is not expected to exceed 0.00 mK. Plateau temperatures of the melting curves for this material are expected to differ by less than 0.01 mK from each other. The ITS-90 melting-point temperature assigned to SRM 1751 is 29.7646 °C with an expanded uncertainty of (k=2) of 0.07 mK A copy of the certificate for SRM 1751 is given in Appendix A.

7. References

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

[2] Glasstone, S., *Thermodynamics for Chemists*, p. 322, (D. Van Nostrand Co., Inc., New York, 1947).

[3] Strouse, G.F., “NIST Methods of Estimating the Impurity Uncertainty Component for the ITS-90 Fixed-Point Cells from the Ar TP to the Ag FP, ” 2003, CCT 03-19.

[4] Mangum, B.W., Thornton D.D., “Determination of the triple-point temperature of gallium”, Metrologia, 1979, **15**, pp. 201-215.

[5] Mangum, B.W., “Triple point of gallium as a temperature fixed point”, Temperature: Its Measurement and Control in Science and Industry, edited by J.F. Schooley, 1982, **5,** pp. 299-309.

[6] Strouse G.F., “NIST Realization of the Gallium Triple Point”, Tempmeko ’99: The 7th International Symposium on Temperature and Thermal Measurements in Industry and Science, edited by J. F. Dubbledam and M. J. Groot, 1999, pp.147-152.

[7] Arai, M., Sakurai, H., “Stability study on the gallium triple point using sealed glass cells”, Temperature: Its Measurement and Control in Science and Industry, edited by J.F. Schooley, 1992, **6,** pp. 315-318.

[8] Strouse, G.F., "NIST Implementation and Realization of the ITS-90 Over the Range 83 K to 1235 K. Reproducibility, Stability, and Uncertainties," *Temperature. Its Measurement and Control in Science and Industry,* Edited by J.F. Schooley, Vol. 6, pp. 169-174, (American Institute of Physics, New York, 1992).

[9] Kaeser, R.S., and Strouse, G.F., “An ITS-90 Calibration Facility”, NCSL Conference Proceedings, 1994.

[10] Strouse, G.F., “Thermal Characteristics of the NIST Fixed-Point Cells, Furnaces, and Maintenance Baths over the Temperature Range from 83.8058 K to 1234.93 K”, Tempmeko ’99: The 7th International Symposium on Temperature and Thermal Measurements in Industry and Science, edited by J. F. Dubbledam and M. J. Groot, 1999, pp.153-158.

[11] ISO, Guide to the Expression of Uncertainty in Measurement, International Organization for Standardization, Geneva, Switzerland, 1993.

[12] B.N. Taylor and C.E. Kuyatt, "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, 17 pp. (1993).

8. Appendix A

Certificate for SRM 1751: Ga MP standard.

UNDER CONSTRUCTION

CONTENTS

PAGE