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U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

Standard Reference Materials:

Application of Some Metal SRM's as Thermometric Fixed Points

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CERTIFICATES AND ANALYSES OF STANDARD REFERENCE MATERIALS AND RESEARCH MATERIALS

Application of Some Metal SRM's as Thermometric Fixed Points

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Abstract

Equipment and procedures are described for the realization of liquid-solid phase equilibrium states of some pure metals as thermometric fixed points for platinum resistance thermometry. The design and techniques for assembling fixed-point cells using Standard Reference Materials (SRM) 740 (zinc), 43h (zinc), 42g (tin), 741 (tin), 44f (aluminum), 746 (cadmium), and 743 (mercury) are given and the results of the measurements using the purer of these metal SRM's are analyzed and evaluated. The reproducibility of temperature measurements with these metal SRM's is shown to be about ± 0.1 mK.

Key words: Aluminum point; cadmium point; check thermometers; freezing point; melting point; mercury point; phase equilibrium; standard platinum resistance thermometer (SPRT); thermometric fixed point; tin point; triple point; zinc point.

Disclaimer

In order to adequately describe materials and experimental procedures, it was occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Bureau of Standards nor does it imply that the particular products or equipment is necessarily the best available for that purpose.

1. Introduction

The current internationally adopted temperature scale is the International Practical Temperature Scale of 1968 (Amended Edition of 1975) [36][1], henceforth in this publication to be designated as IPTS-68. The IPTS-68 is based on the assigned values of the temperatures of specified equilibrium states of pure substances (i.e., defining fixed points) and on standard instruments calibrated at these temperatures. Between the fixed-point temperatures, interpolation equations relate the indications of the standard instruments to temperature values of the IPTS-68. The platinum resistance thermometer is the specified standard instrument from 13.81 K (-259.34°C) to 903.89 K (630.74°C), the platinum-10% rhodium alloy versus platinum thermocouple from 903.89 K to 1337.58 K (1064.43°C), and the optical pyrometer above 1337.58 K. (A platinum resistance thermometer that meets the IPTS-68 specifications for a standard will, henceforth, be designated as a standard platinum resistance thermometer or simply as a SPRT.)

The assigned values of temperature of the thirteen defining fixed points of the IPTS-68 are listed in Table I; nine substances are involved. In addition to the defining fixed points, the IPTS-68 document [36] lists thirty-one other equilibrium states designated as secondary reference points which involve twenty-nine substances, four of these substances being used also for the equilibrium states of the defining fixed points. Recently, the Consultative Committee for Thermometry (a subcommittee of the International Committee of Weights and Measures) published an extended list of sixty-one secondary reference points involving thirty-six different substances [4]. This extended list is given in Table II. Where more than one value of temperature was given for the equilibrium state, an average value is given in Table II. The vapor pressure versus temperature relations given for some of the substances in the compilation are omitted from Table II.

The secondary reference points are useful in certain measurement situations, e.g., for checking the calibration of SPRT's and secondary thermometers, particularly in the temperature range where they are to be used. The secondary reference points may be used also for direct calibration of thermometers, if certain limitations are recognized. If an SPRT is calibrated using secondary reference points to obtain the coefficients of the specified form of the IPTS-68 interpolation equation, the interpolation equation should be expected to deviate somewhat from an interpolation equation that would be obtained if the SPRT were calibrated according to the IPTS-68 specifications. The temperature value that is assigned to a secondary reference point is usually an average of a number of measurements with different SPRT's calibrated in terms of the IPTS-68 and of a number of realizations of the reference point. The uncertainties of calibration using secondary reference points will include, in addition to the local uncertainties of measurements and

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[1] Figures in brackets indicate the literature references listed at the end of this publication.

Table I

Defining Fixed Points of the IPTS-68[a]

Substance and equilibrium state[b]	Assigned value of the IPTS-68 temperature	
	T,K	t,°C
e-H_2^c, TP	13.81	-259.34
e-H_2^c, BP[d] (33,330.6 Pa)	17.042	-256.108
e-H_2^c, BP[d]	20.28	-252.87
Ne, BP[d,e]	27.102	-246.048
O_2, TP	54.361	-218.789
Ar, TP[f]	83.798	-189.352
O_2, CP[d]	90.188	-182.962
H_2O, TP	273.16	0.01
H_2O, BP	373.15	100
Sn, FP[g]	505.1181	231.9681
Zn, FP	692.73	419.58
Ag, FP	1235.08	961.93
Au, FP	1337.58	1064.43

[a] Except for the triple points and the equilibrium hydrogen point at 17.042 K, the assigned values of temperature are for equilibrium states at a pressure of 101,325 Pa (1 standard atmosphere). In the realization of the fixed points, small departures from the assigned temperatures occur as a result of small deviations from the specified pressure at the point of immersion of the thermometer. Adjustment is made for these small temperature differences.

[b] TP = triple point, BP = boiling point, CP = condensation point, FP = freezing point, and e-H_2 = equilibrium hydrogen.

[c] Hydrogen has two molecular configurations (nuclear spin arrangements), designated ortho and para. The equilibrium composition is temperature dependent. Equilibrium hydrogen means that the hydrogen has its equilibrium composition at the relevant temperature.

Table I (continuation)

[d] Fractionation of isotopes or impurities dictates the use of boiling points (vanishingly small vapor fraction) for hydrogen and neon, and condensation point (vanishly small liquid fraction) for oxygen.

[e] The neon used should have the normal isotopic composition: 0.905 mol ^{20}Ne, 0.092 mol ^{22}Ne, and 0.0027 mole ^{21}Ne.

[f] The triple point of argon may be used as an alternative to the condensation point of oxygen.

[g] The freezing point of tin (t' = 231.9292°C) may be used as an alternative to the boiling point of water.

Table II

Secondary Reference Points[a]

Equilibrium State[b,d]	IPTS-68 Temperature	
	T,K	t,°C
n-H_2, TP	13.957	-259.193
n-H_2, BP	20.397	-252.753
O_2, TR(α-β)	23.867	-249.283
Ne, TP	24.561	-248.589
O_2, TR(β-γ)	43.801	-229.349
N_2, TP	63.146	-210.004
N_2, BP	77.344	-195.806
Ar, BP	87.294	-185.856
CH_4, TP	90.686	-182.464
Kr, TP	115.770	-157.380
Kr, BP	119.800	-153.350
Xe, TP	161.388	-111.762
Xe, BP	165.060	-108.090
CO_2, SP	194.674	-78.476
CO_2, TP	216.580	-56.570
Hg, TP	234.308	-38.842
Hg, FP	234.314	-38.836
Ice point[c]	273.15	0
Phenoxybenzene, TP	300.011	26.861
Ga, MP	302.921	29.771
Benzoic acid, TP	395.52	122.37
In, FP	429.784	156.634
Bi, FP	544.592	271.442
Cd, FP	594.258	321.108

Table II (continuation)

Pb, FP	600.652	327.502
Hg, BP	629.81	356.66
S, BP	717.824	444.674
Cu-Al eutictic, MP	821.41	548.26
Sb, FP	903.905	630.755
Al, FP	933.607	660.457
Cu-Ag eutectic, FP	1052.75	779.60
Cu, FP	1358.03	1084.88
Fe, RT of M	1670	1397
Ni, FP	1728	1455
Co, FP	1768	1495
Fe, MP	1808	1535
Pd, FP	1827	1554
Zr, RT of M	1940	1667
Pt, FP	2042	1769
Zr, MP	2128	1855
Rh, FP	2236	1963
Al_2O_3, MP	2327	2054
Nb, RT of M	2425	2152
Mo, RT of M	2531	2258
Ir, FP	2720	2447
Nb, MP	2746	2473
Mo, MP	2896	2623
W, MP	3695	3422

[a] The temperatures listed are the best values at the time of compilation.

[b] The equilibrium states in the table are at a pressure of 101,325 Pa (1 standard atmosphere) except for the triple points.

Table II (continuation)

[c] The ice point is a very close approximation to the temperature defined as being 0.01 K below the triple point of water.

[d] TP = triple point, BP = boiling point, SP = sublimation point, FP = freezing point, MP = melting point, TR = solid phase transition point, RT of M = radiance temperature of the melting metal, and $n\text{-}H_2$ = normal hydrogen (the high temperature equilibrium composition of ortho and para hydrogen, closely approached at room temperatures, consisting of a mixture of 75% orthohydrogen and 25% parahydrogen).

realizations of the secondary reference points, the errors of assignment of temperature values to the secondary reference points and the differences in the SPRT's. Also, in such calibrations the range of the temperatures of the secondary reference points used is, in general, less than the range of the defining fixed points of the IPTS-68; hence, the resulting interpolation equation that is obtained is expected to be of lower accuracy than the interpolation equation from a regular calibration. Any extrapolation of the equation beyond the range of the calibration points should be expected to give even larger errors. (See reference [31] for analysis of propagation of errors when temperatures are extrapolated above the zinc point, even though the calibration is in accordance with the IPTS-68.)

For thermometers (other than SPRT's) that are calibrated using the fixed points, the interpolated values of temperature between the calibration points should be expected to be different from those of the SPRT's, again depending upon the range of interpolation. The calibration of such thermometers should be at small enough temperature intervals so that the temperature derivative of the thermometer scale is close enough to that of the SPRT for the application. Industrial type platinum resistance thermometers, because of their construction (which is not strain free or free of possible chemical contamination), should be expected to behave differently from SPRT's.

The large number of substances given in Tables I and II shows that a wide variety of pure substances is needed for accurate thermometry. Some of these substances are available from the National Bureau of Standards - Office of Standard Reference Materials (NBS-OSRM). Among the thermometric fixed points, the realization of liquid-solid phase equilibrium states is relatively less complicated than the liquid-vapor phase equilibrium states because the effect of pressure on the temperature of the former is relatively smaller. Metals have the additional advantage of having high thermal conductivity which promotes rapid temperature equilibrium. This paper deals with the application of some of the available metal standards that are suitable for the calibration and testing of SPRT's.

A number of high-purity metals suitable for thermometric freezing-point (or melting-point) standards can be obtained as Standard Reference Materials (SRM) from the NBS-OSRM [39]. The calibration or testing of SPRT's usually requires relatively large samples (about 130 to 180 cm^3) in the freezing-point cells [16,25]. The SPRT must be immersed sufficiently in the sample to provide measurements that are independent of the ambient temperature. Moreover, with certain AC bridge [6] or DC current comparator bridge [22], the SPRT (of R(0°C)=25.5 ohm) can give measurement resolutions that correspond to better than 0.01 mK with systems that have high thermal stability. At these high measurement resolutions, not only must the immersion of the SPRT be adequate but also an accurate information on the relative location of the SPRT resistor coil and the liquid surface of the freezing-point cell must be available to correct for the hydrostatic head with an accuracy consistent with the measurement precision.

Similarly, wherever applicable, adjustments for variations in the barometric pressure must also be made or, better still, the pressure in the freezing-point cell be controlled to 1 atm. Table III lists the effect of pressure and hydrostatic head on the freezing point for some of the substances.

There is a practical limitation on the height (depth of immersion) to which the cell containing the metal could be made. However, the apparent depth of immersion in the thermometric cell can be increased by suitably tempering the thermometer stem above the cell to a temperature close to that of the cell [13,27,31]. The adequacy of immersion of the SPRT should always be tested by measuring the thermometer resistance at two or more depths of immersion in the cell (e.g., at maximum immersion and at a few cm less). The temperature readings must be consistent with the difference due to the effect of hydrostatic head of the liquid metal. With a relatively large sample and precise temperature control at about 1 K below the freezing point, total freezing times of 14 to 20 hours can be achieved using a relatively simple tube furnace to contain the cell. Longer freezing times can be obtained by controlling the furnace temperature closer than 1 K below the freezing temperature. This paper describes the procedures that have been employed, in the Platinum Resistance Thermometry Laboratory of the NBS, in the assembly of freezing-point cells with metal standards from the NBS-OSRM for use with long-stem type (or immersion type) SPRT's. In particular, procedures are described for assembling cells of zinc, tin, aluminum, cadmium, and mercury. However, similar procedures can be employed in assembling cells of indium, lead, antimony, bismuth, silver, gold, and other metals that can be melted in graphite crucibles. [Gallium melting-point standard (SRM-1968), designed for calibration of miniature temperature probes, such as thermistors and thermocouples, is available from the NBS-OSRM packaged in plastic holders suitable for immediate application using a thermostated bath [38].]

The zinc point and the tin point are defining fixed points of the IPTS-68; they are used regularly for the calibration of SPRT's in the Platinum Resistance Thermometer Laboratory (henceforth, to be designated simply as PRTL) of the NBS. The aluminum point and the mercury point are being considered as additional fixed points to better define the future new IPTS. The cadmium point has been selected for verifying the SPRT calibrations at the triple point of water, the zinc point, and the tin point. The accuracy of the calibration can be checked within a few tenths of a millikelvin from the measurements at the cadmium point. Although the realization of the indium point is not described in this report, it will be investigated in the near future for application in the verification of the SPRT calibrations. This report describes procedures used in the PRTL of the NBS for realizing the freezing points of the metals. The observed freezing curves of the metals and the results of repeated measurements of SPRT's during a single freeze of the metal (except aluminum) are shown.

Table III

Effect of Pressure on the Temperatures of Some Defining Fixed Points and Secondary Reference Points of the IPTS-68

Substance and Equilibrium State[a]	Equilibrium Temperature T,K	Pressure Coefficient mK per std atm	Pressure Coefficient mK per meter of liquid
e-H_2, TP	13.81[b]	34	0.25
O_2, TP	54.361[b]	12	1.5
Ar, TP	83.798[b]	25	3.3
H_2O, TP	273.16[b]	-7.5	-0.7
Sn, FP	505.1181[b]	3.3	2.2
Zn, FP	692.73[b]	4.3	2.7
Ag, FP	1235.08[b]	6.0	5.4
Au, FP	1337.58[b]	6.1	10
Ne, TP	24.561[c]	16	1.9
Hg, FP	234.314[c]	5.4	7.1
Ga, TP	302.9241[d]	-2.0[d]	-1.2[d]
In, FP	429.784	4.9	3.3
Bi, FP	544.592	-3.5	-3.4
Cd, FP	594.258[c]	6.2	4.8
Pb, FP	600.652[c]	8.0	8.2
Sb, FP	903.905[c]	0.85	0.5
Al, FP	933.607[c]	7.1[e]	1.6[e]

[a] TP = triple point, FP = freezing point at 101,325 Pa (1 standard atmosphere).

[b] Defining fixed point of the IPTS-68.

[c] From reference [36].

[d] From reference [23].

[e] From reference [13].

In the paper, the application of the zinc standard is discussed first in the following sequence:

1) the description of the metal standard,

2) the graphite cell to contain the zinc,

3) the filling of the crucible with zinc,

4) the zinc freezing-point cell,

5) the description of the furnace for carrying out the freezing-point measurements,

6) the procedure for carrying out the freezing-point measurements, and,

7) the results of the freezing-point measurements.

The other metal standards that require graphite cells are then described in the order: tin, aluminum, and cadmium. References are made to the descriptions given for zinc, or for any other metal that was discussed earlier, wherever the equipment or the procedures are identical or sufficiently similar. The application of the mercury standard, which follows an entirely different procedure from those of the other metals, is described in full separately.

2. Zinc Freezing Point

The state of thermodynamic equilibrium between solid and liquid zinc at 1 standard atmosphere of pressure is a defining fixed point of the IPTS-68 with an assigned value of 419.58°C (692.73 K); henceforth, it will be referred to as the freezing point of zinc or, simply, the zinc point. Because of the greater reproducibility and ease of realization of the zinc point over the sulfur point (normal boiling point of sulfur), the use of the zinc point was recommended in place of the sulfur point in the text revision of the International Practical Temperature Scale of 1948 [34]. In the IPTS-68 [36] the zinc point replaced the sulfur point and the sulfur point was placed among the secondary reference points. Prior to 1966 the sulfur point was maintained at the NBS for the calibration of SPRT's (see reference [33]); since 1966 the zinc point has been maintained instead.

2.1 Zinc Samples

Zinc freezing-point samples are available from the NBS-OSRM in two different levels of purity; one sample designated SRM-740 (see Appendix A) is nominally 99.9999 percent pure and the other sample designated SRM-43h (see Appendix B) is nominally 99.999 percent pure. The SRM-740 zinc (supplier lots HPM 5815, 6003, and 6071)[2] is of exceptionally high purity; it is used at the NBS to realize the defining fixed point, i.e., the freezing point of pure zinc, as specified on the IPTS-68. The material was prepared by double vacuum distillation of commercial electrolytic grade zinc, the yield being approximately 70 percent. The purified material was then melted in a graphite crucible and poured into graphite boats for zone refining. Twenty zone refining passes were made in air after which the "leading" and the "trailing" ends of the bar were cropped, the yield from this process being approximately 60 percent. The zone refined bars were homogenized and finally, to degassify the material, were given a gradient freeze under hydrogen gas. The gradient freeze process involved melting the sample in a fused quartz boat by heating in a furnace with eight zones; when completely melted, the heat to the zones was turned off sequentially, one per hour. Approximately 3 cm were cropped from each end of the bars. The final bars were semi-cylindrical (5 cm across the flat) and about 68 cm long.

Assay values, based on emission spectrochemical analysis, that accompanied the zinc bars from the supplier (from which SRM-740 samples were prepared by cutting and cleaning) are listed in Table IV. Emission spectrochemical analysis at NBS of two specimens from lot HPM 5815 is summarized in Table V. Table VI summarizes mass spectrochemical analyses on specimens from lots HPM 5815 and 6003. The emission spectrochemical analyses from the NBS and from the supplier are in good agreement.

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[2] The NBS-OSRM obtained from the supplier 458 kg of nominally 99.9999 percent zinc in three lots: HPM 5815, 6003, and 6071. The lot HPM 5815 consisted of 33 bars weighing a total of 164 kg, lot HPM 6003 of 32 bars weighing 158 kg, and lot HPM 6071 of 27 bars weighing 136 kg (NBS Order No. S-440757-66, Contract No. CST-122).

Table IV

Emission Spectrochemical Analysis of the Zinc Samples (From the Assay Certificates of Supplier, by Analysis of the "Master Sample")

Element	Sample (Lot HPM) 5815[a]	6003[b] (in ppm)	6071[c]
Ca	0.1	<0.1	
Cu	<0.1	0.1	<0.1
Fe	0.2	0.3	0.3
Mg	0.1	<0.1	<0.1
Pb		0.2	0.3
Sb	0.1	0.1	0.1
Si	0.1	0.1	0.1

[a] Date: October 29, 1965.

[b] Date: December 23, 1965.

[c] Date: January 20, 1966.

Table V

Emission Spectrochemical Analysis of the Zinc Samples[a]

(SRM-740, Lot HPM 5815, Bars 1 and 33)

Impurity elements detected and estimated concentrations in ppm:

Ag <0.1, Cd <0.1, Cu <0.1,

Fe 0.2, Mg <0.1

Presence of Si questionable, if present, does not exceed 0.2.

Estimated limits of detection in ppm and the elements sought and not detected:

<0.1	Be
0.2	Bi, Pb, Ca, Cr, Co, Mn, Ni, Sn, V
0.5	Al, Au, Ca, B, Ge, In
1.0	Sb

[a] Analysis by R. Alvarez of Spectrochemical Analysis Section, National Bureau of Standards, (March 7, 1966).

Table VI

Mass Spectrochemical Analysis of the Zinc Samples (SRM 740, Lots HPM 5815 and 6003)

Lot HPM	5815	5815	5815	5815	6003	6003
Bar and Specimen No.	1A2	1B2	33A2	33B2	34T2	34L2
Detection Limit[b] (Atomic ppm)	0.0052	0.0054	0.0076	0.0190	0.0090	0.0046
Elements Found (ppm by weight)						
Pb	<0.04	<0.04	<0.04	0.6	<0.07	<0.04
W	<0.08	<0.06	0.3	<0.1	<0.06	0.3
Cd	<0.04	<0.04	0.05	<0.1	0.9	0.04
Ni	0.08	0.05	0.06	0.3	0.08	0.02
Fe	0.06	0.04	0.05	0.07	0.06	0.05
Cr	0.05	0.01	0.01	0.03	0.02	0.01
Ca[c]	0.003	0.004	0.006	0.006	0.001	0.007
K[c]	0.009	0.016	0.03	0.03	0.01	0.03
Cl[c]	0.03	0.4	0.1	0.2	0.06	0.05
Al[c]	0.007	0.005	0.004	0.01	0.01	0.004
Na[c]	0.009	0.01	0.01	0.03	0.01	0.03
Limits of Detection of Elements that Interfere. These elements were not detected at these limits (ppm by weight)						
Au	23	5	7	5	18	7
Pt	0.6	0.1	0.2	0.1	1	0.1
Ta	400	3	200	20	80	450
Ba				0.7	0.07	
Cs				0.6	0.9	
Nb	0.2	0.2	0.1	0.1	0.3	0.1
Se	0.04	0.04	0.1	0.07	0.16	0.06
Ga	2.5	1.6	0.6	70	2	2
Cu	400	40	13	1300	20	5
Co	0.01	0.08	0.03	0.02	0.1	0.01
				0.03	0.04	
Ti				0.2	0.1	
S	100	20	13	70	30	40
Si	0.1	0.1	0.05	0.4	0.3	0.06
Mg	0.002	0.002	0.001	0.001	0.0003	0.001
O	0.5	3	6	20	1	0.05
N	30	20	15	50	10	20
C	1.5	0.7	1	2	1.5	1
Li	0.0001	0.0001	0.0001	0.0004	0.0001	0.0001

[a] Analysis was performed by P.J. Paulsen and P.E. Branch, Analytical Chemistry Division, National Bureau of Standards (March 17, 1966).

[b] To convert the atomic ppm detection limit to ppm by weight detection limit for any element, multiply by the ratio of the atomic weight of the element to that of zinc. Elements not listed are at a concentration below the atomic ppm detection limit given.

[c] These elements appeared to be surface contamination.

However, the mass spectrochemical analysis shows elements such as Ca, Fe, Mg, and Pb to be less than that found by the emission spectrochemical analyses. The results of the neutron activation analysis given in Table VII are consistent with those of the emission and mass spectrochemical analyses. R.L. Powell (at the time with the Cryogenic Properties of Solids Section of the NBS at Boulder, Colorado) found the residual resistivity ratios (RRR, ratio of the resistivity at 0°C to that at 4.2K) of samples from the opposite ends of two bars, on which the emission spectrochemical analyses were also made, to range from 33,000 to 38,000 [29]. From the results of the various analyses the purity of the SRM-740 zinc has been estimated to be better than 99.9999 percent.

The SRM-740 zinc samples are available in 350-g units. They were cut "dry" from the final bars with a carbide-tipped cutter in such a manner that only the carbide tip came into contact with the zinc bar. The bars were handled using polyethylene gloves and were held in the milling machine through a polyethylene cover. After cutting, the samples were etched in high-purity dilute nitric acid, rinsed with distilled water, and then air dried. Finally, they were sealed in polyethylene bags. (See SRM-740 certificate, Appendix A.)

Depending upon the graphite crucible used for the zinc-point cell, the mass of zinc required to properly fill the crucible was either 1210 g or 1160 g. The graphite crucible is filled with enough metal so that the upper surface of the liquid metal, when a few degrees above the melting point, would be between 1 and 5 mm below the lower surface of the crucible lid with the well inserted. When the 350-g SRM-740 units were used to fill the cells, three units plus a suitable fraction of the fourth unit were needed. Thus, additional cutting of the zinc was required. In other cases the samples for the zinc-point cells were cut directly from the SRM-740 source bars. In both cases the cut samples were cleaned as described above.

The zinc bars for SRM-43h (Appendix B) were prepared by casting commercial electrolytic grade zinc in a manner similar to that described for the SRM-740 zinc. The material was received from the supplier in three lots (HPM 6576, 6577, and 6592) totaling approximately 454 kg. The semi-circular bars were cut and cleaned to form the 350-g SRM-43h units. The zinc from these lots is issued also as SRM-683. (See SRM-683 certificate for information on the purity of SRM-43h zinc, Appendix C.)

2.2 Graphite Cells for Containing Metals

Graphite is sufficiently chemically inert to contain many metals that melt above 100°C (In the case of mercury, which melts near -39°C, both borosilicate glass and type 304 stainless steel cells are being used; see Section 6.2). The graphite for fabricating the crucibles and assembled parts comprising the cells must be highly pure, sufficiently dense (at least 1.76 g/cm^3), and free of voids and cracks. After fabrication, the graphite parts must be cleaned of metal impurities that may have been introduced during the machining process. There are a number of

Table VII

Neutron Activation Analysis of the Zinc Sample[a]

Element	Lot HPM[b] (in ppm)
Cd	<0.16
Au	<0.006
Ag	<0.10
Na	<0.004

[a] Analysis by G.R. Smith, Analytical Chemistry Division, National Bureau of Standards (March 1, 1966).

[b] Analysis report does not differentiate whether the sample was HPM 5815, HPM 6003, or HPM 6071.

fabricators of graphite equipment in the United States that can provide the graphite and machine and clean the cell parts ready for filling.

The finished graphite cell should be handled as being very fragile and it should be thoroughly inspected for defects before filling. It is difficult to detect defects, such as cracks and voids, in the graphite. At elevated temperatures minute openings in the graphite may become more pronounced. On occasions molten metal has seeped through crucibles that otherwise appeared perfectly sound. A graphite cell in which one metal leaked through might have been perfectly suitable for another metal that melts at a lower temperature or has a higher viscosity. Hence, during filling and during use, one should be prepared for the possible leakage of hot liquid metal through the graphite. Before filling, the graphite crucible and associated parts should be first baked in high vacuum at least 200°C above the melting point of the metal to be filled to remove any volatile impurities.

The dimensions of graphite crucibles, lids, and thermometer wells that are used at the NBS are shown in Figures 1, 2, and 3 (also, in Figures 16 and 17). The outside diameter of the crucible has been standardized to 43.7 ± 0.1 mm so that the crucible can be inserted inside cylindrical glass holders that are nominally 45 to 48 mm inside diameter.

The crucible shown in Figure 1 has been used with both thermometer well and lid assemblies of Figures 2 and 3. The screw threads of the lid and thermometer well of Figure 2 have been cut so that the two can be "snugly" assembled. The enlarged radius below the screw threads on the thermometer well serves to strengthen the well near its junction with the lid. (Although more graphite must be machined, the lid and thermometer well could be fabricated as one piece instead of two pieces as shown in Figures 2 and 3.)

Above 200°C or so, the graphite must be protected from air to avoid oxidation. The protective holder for the graphite cell is designed so that it could be handled with the cell still hot and also could contain inert gas at a pressure slightly above that of the ambient. The protective enclosure for the graphite cell could be stainless steel or a high chromium-nickel alloy, such as Inconel[3]. However, to avoid possible contamination of the metal sample inside the graphite cell by particles of the metal holder that could become loose, a borosilicate glass or fused-quartz glass is used at the NBS to contain the graphite cell. Figure 4 shows the dimensions of the borosilicate-glass holder used with graphite cells containing zinc, tin, or cadmium.

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[3] Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

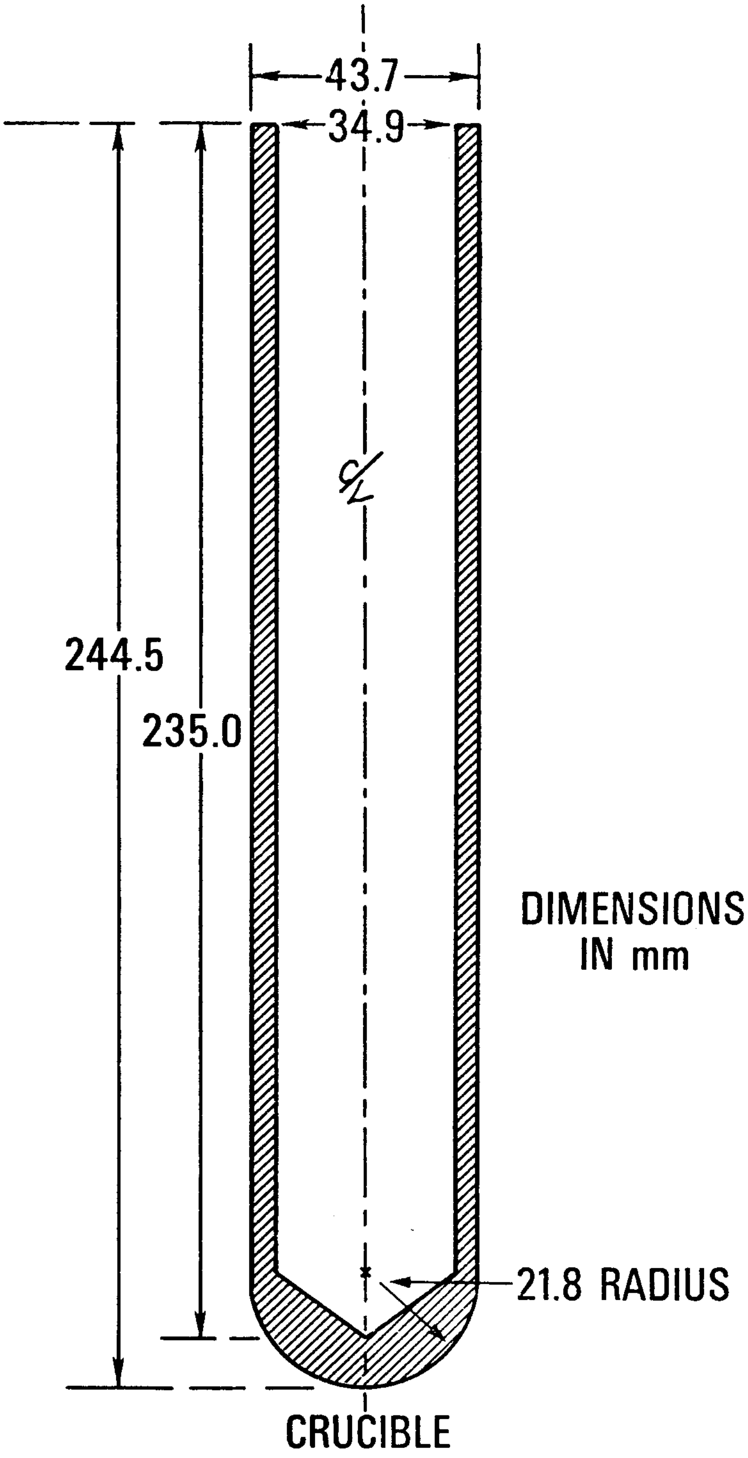


Figure 1. Graphite crucible for containing metal samples used in freezing-point measurements.

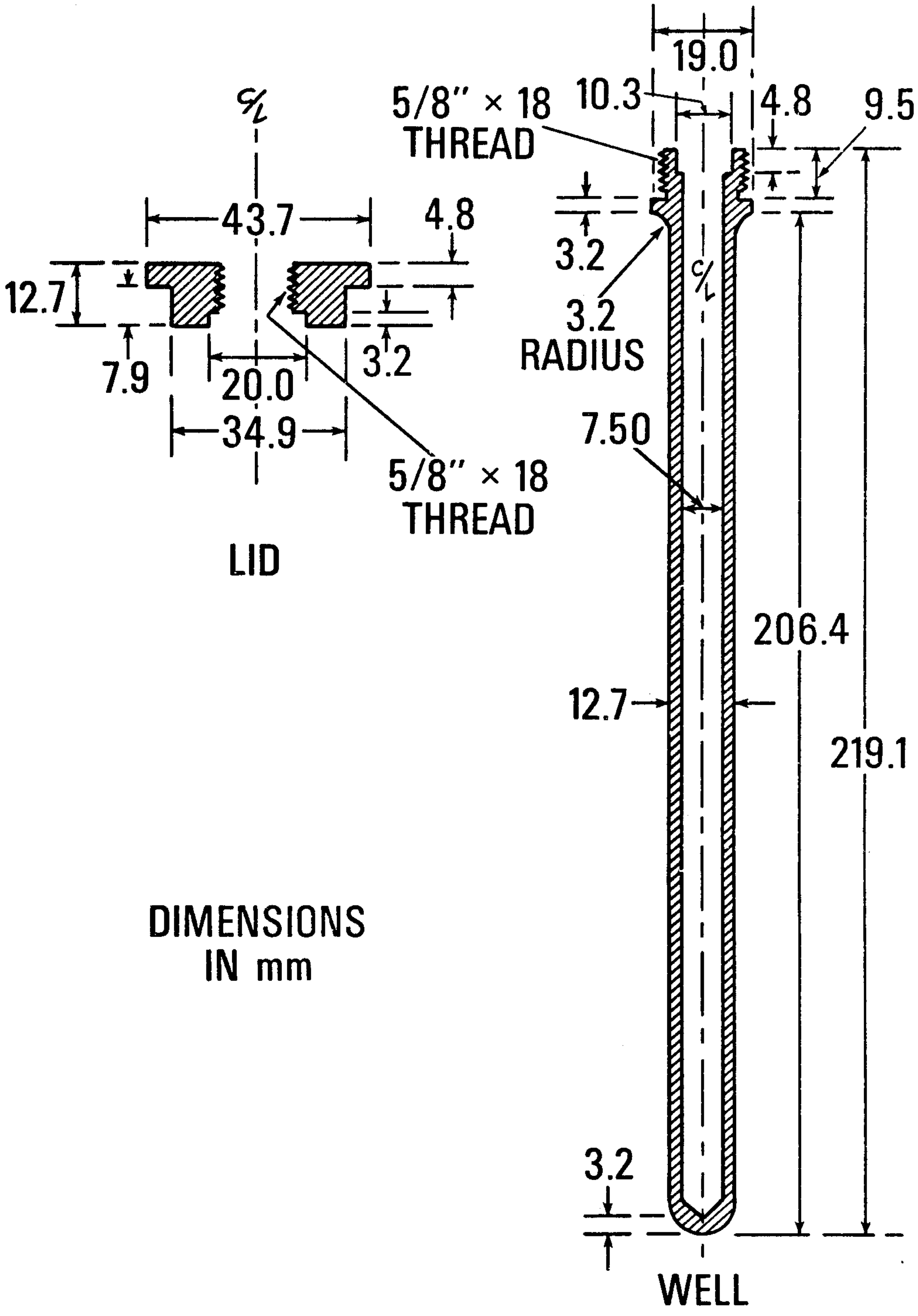


Figure 2. Graphite lid and thermometer well (threaded type for crucible of Fig. 1.

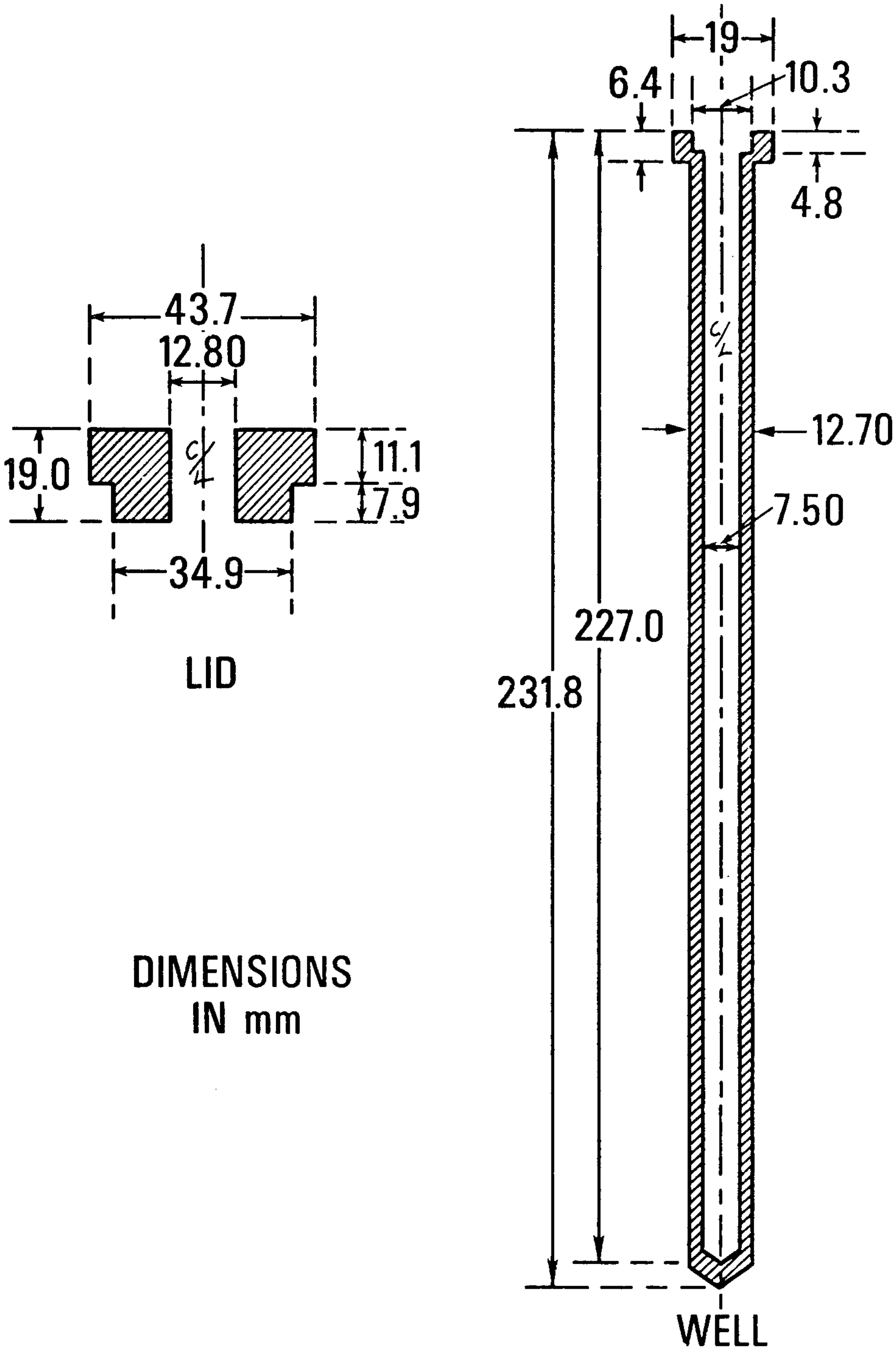
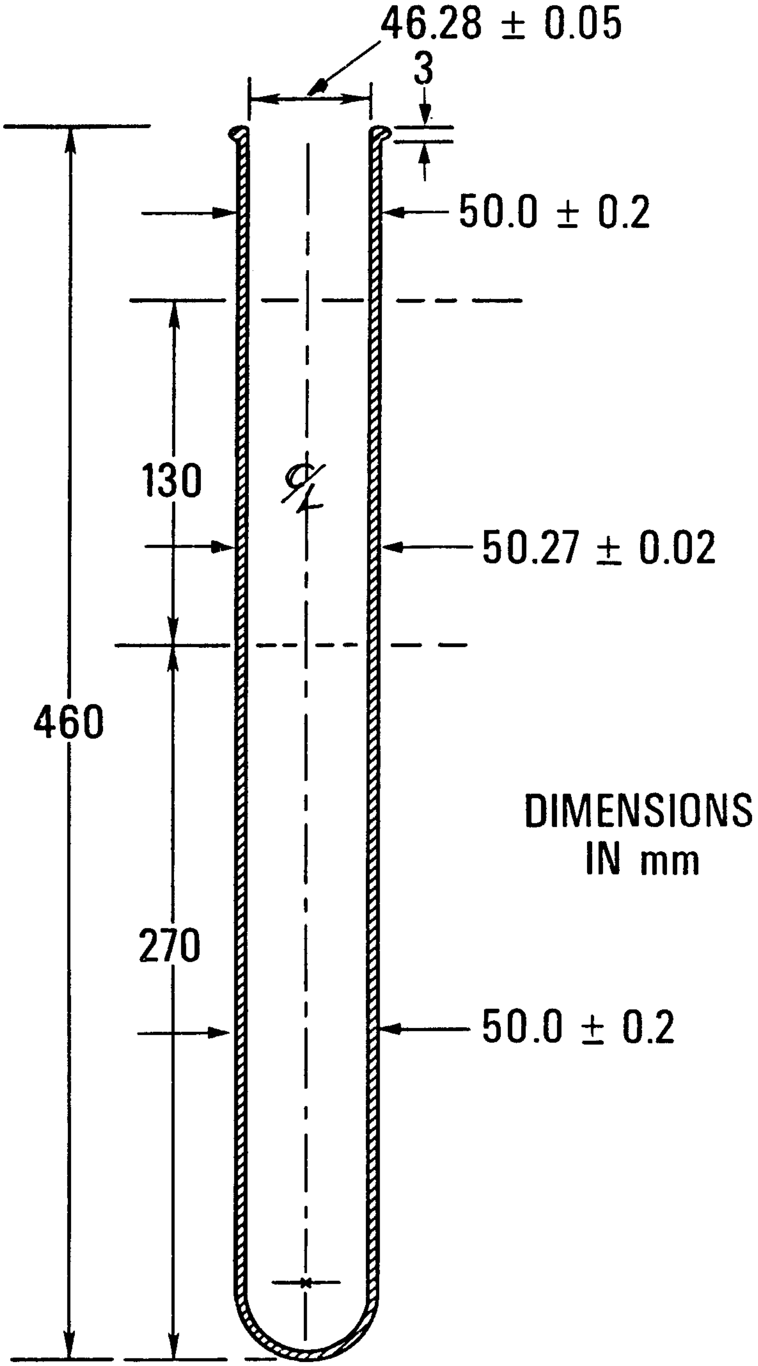


Figure 3. Graphite lid and thermometer well (slide-through type) for crucible of Fig. 1.



BOROSILICATE–GLASS TUBE

Figure 4. Borosilicate-glass tube used to house the graphite crucible assembly with metal (tin, cadmium, or zinc) for freezing-point measurements (see Fig. 9). The tube was made from precision bore tubing and ground on the outer surface to the indicated diameter.

2.3 Filling Graphite Cells with Zinc

Figure 5 shows the bell-jar equipment arrangement that was used to fill the graphite crucibles with zinc samples. The graphite funnel, C, used for holding the zinc to be melted into the crucible is shown in detail in Figure 6. Since zinc has a relatively high vapor pressure (about 20 Pa [28]) at its melting point, about 0.3 atm pressure of purified argon gas was introduced into the bell jar space while the zinc sample was being melted into the graphite crucible. The graphite crucible and the funnel with the zinc sample (see Figure 5) were first evacuated at about 200°C for an hour; then argon gas was introduced and the induction heating power was raised to melt the zinc into the crucible as quickly as possible to minimize the evaporation loss of zinc. A 5-kW, 450-kHz generator was employed for the induction heating power source. After the start of melting, about 15 minutes were usually required to completely melt the zinc sample in the funnel into the crucible. (In spite of the presence of argon gas and rapid melting of zinc into the crucible, a "mirror" of zinc formed on the bell jar wall.) The filled crucible was then allowed to cool nearly to room temperature, the bell jar was filled to atmospheric pressure with purified argon gas, and the graphite crucible containing the now solidified zinc sample was transferred into a special borosilicate tube for inserting the graphite thermometer well and lid assembly (see Figure 7 and Figure 8).

The procedure used for the installation of the lid and thermometer well into the filled crucible depended upon the design of the lid - thermometer well assembly. Where the thermometer well was attached or attachable firmly to the lid (see Figure 2), the arrangement shown in Figure 7 was used. (This graphite cell design was used exculsively with tin and zinc samples). The filled crucible was slipped into the special borosilicate glass tube and the lid-thermometer well assembly was positioned on a push-rod holder as shown in the figure. The glass tube assembly was thoroughly purged with helium gas and then lowered into a tube furnace held at a temperature 15 to 20°C above the melting point of the metal. (The furnace to be employed for the freezing-point measurement itself was used for this purpose). When the metal was completely melted, the glass tube was raised out of the furnace and the thermometer well and lid assembly was smoothly and quickly pushed into place. To make the assembly operation easy, the outside diameters of the crucible and lid were made the same (see Figures 1 and 2) and the inside diameter of the glass tube in the section near the top of the crucible was reduced to only slightly larger (about 0.01 mm) than the outside diameter of the crucible. Hence, this reduced section of the glass tube served to guide and correctly position the lid to cover the crucible. The lid was designed to fit the crucible closely to minimize the possibility of later contamination. Finally, the assembled graphite cell was allowed to cool slowly and later assembled as a freezing-point cell.

For the graphite cell design, in which the thermometer well slipped freely through the center hole in the lid (see Figure 3), the arrangement shown in Figure 8 was used to assemble the thermometer well and lid with

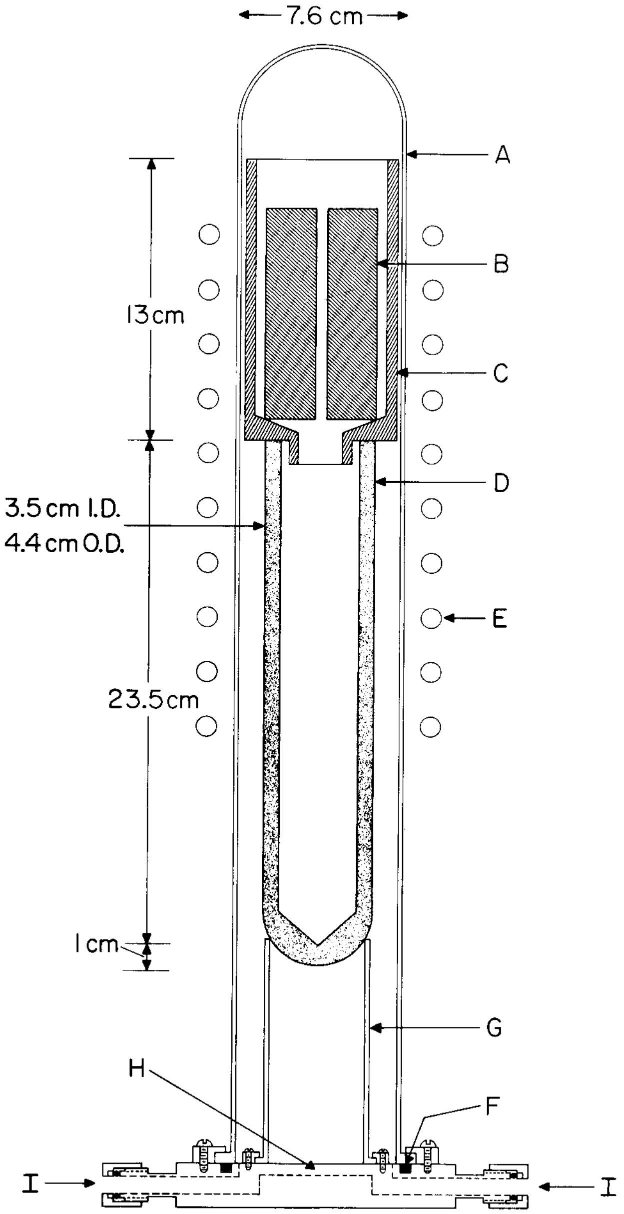


Figure 5. Arrangement for filling the graphite crucible with metal sample by induction heating.

A. Borosilicate-glass envelope.
B. Metal sample.
C. Graphite sample holder and funnel.
D. Graphite crucible.
E. Induction heater coils.
F. "O" ring seal.
G. Borosilicate-glass stand.
H. Slot for pumping out and gas purging.
I. Connection to vacuum and purified argon supply.

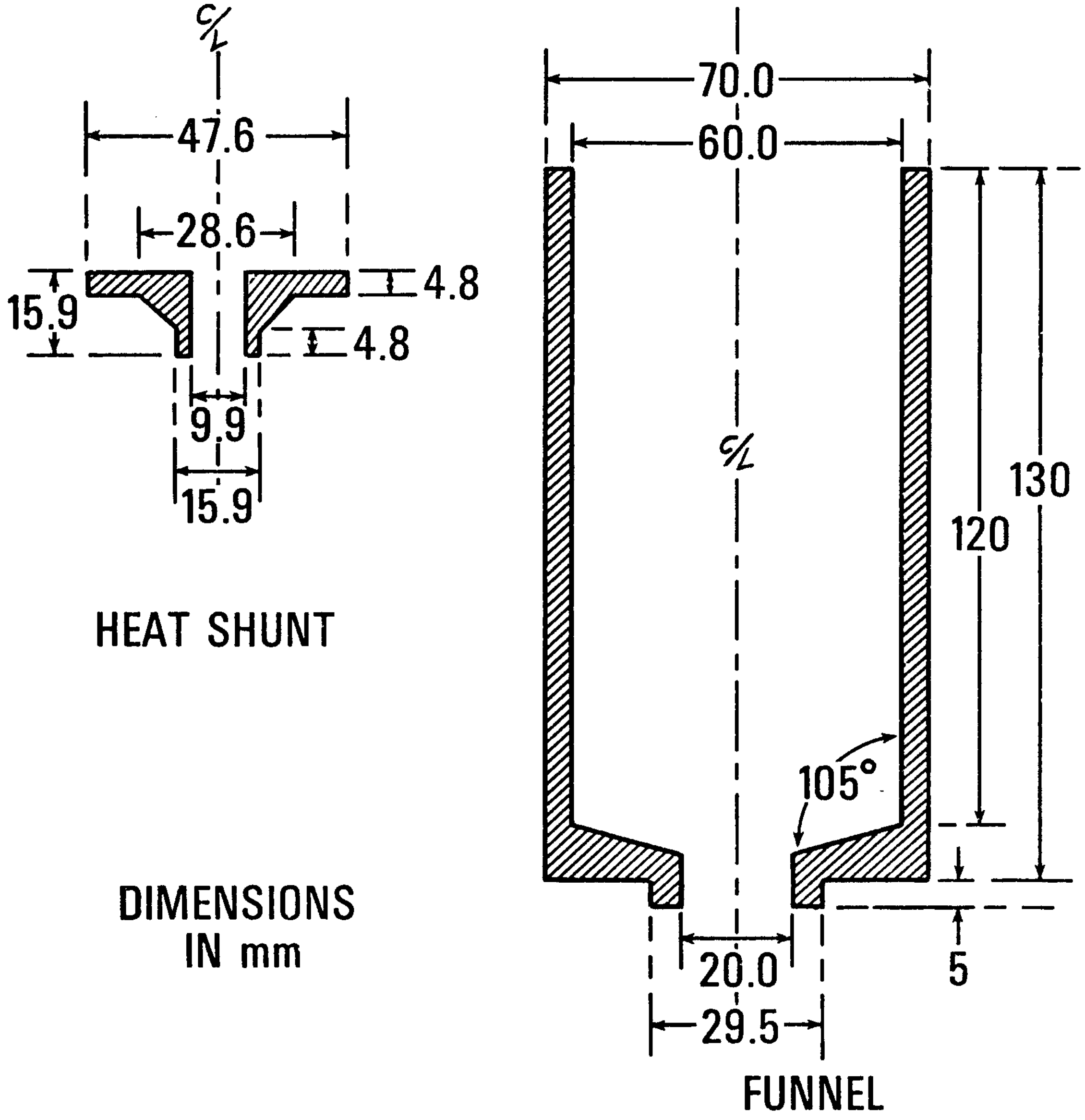
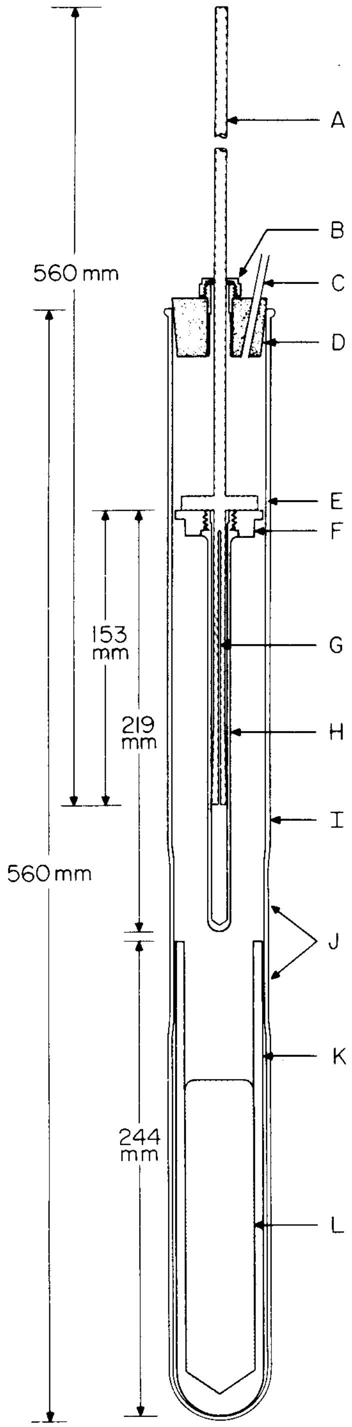
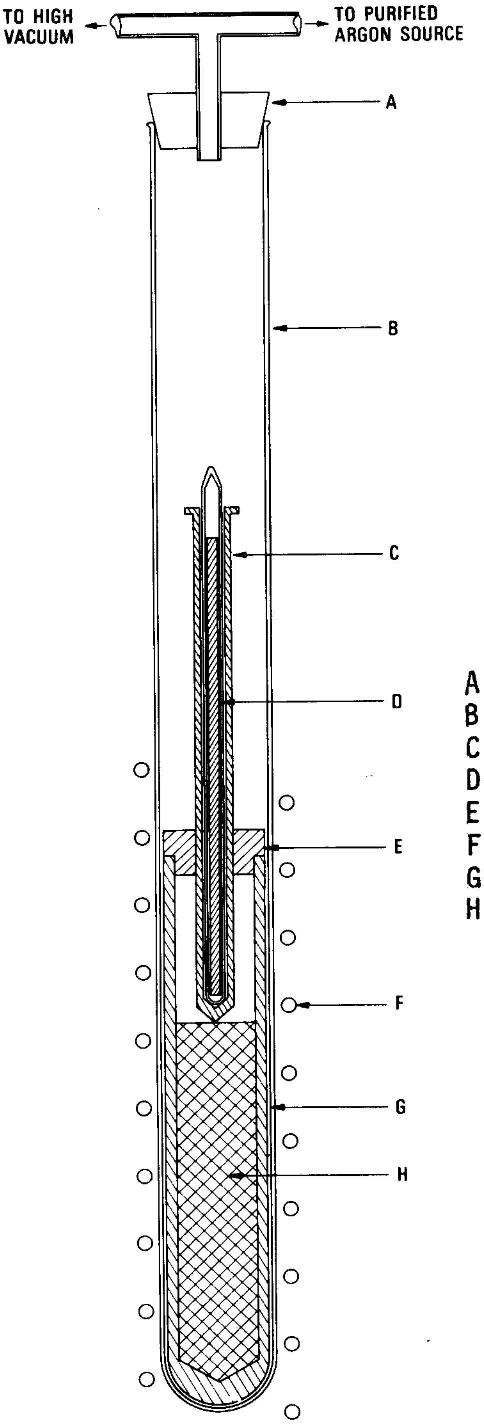


Figure 6. Graphite funnel used to fill graphite crucible with metal sample (see Fig. 5) and graphite heat shunt used in assembling metal freezing-point cell (see Fig. 9).



- A. Stainless-steel pusher rod.
- B. Gas seal with silicone rubber. Permits linear motion of the pusher rod (A).
- C. Inlet for purified helium gas that is used in purging and maintaining positive pressure of the gas during assembly.
- D. Silicone rubber stopper.
- E. Stainless-steel flange attached to the pusher rod for pressing against the graphite lid during assembly.
- F. Graphite lid for the crucible.
- G. Slit on the pusher rod. The two halves are sprung out to hold the graphite thermometer well and lid up while melting the metal sample.
- H. Graphite thermometer well.
- I. Borosilicate-glass tube.
- J. Section of glass tube shrunk to fit the crucible and lid so that lid can be easily guided onto the crucible.
- K. Graphite crucible.
- L. Molten metal sample.

Figure 7. Apparatus and method for installing graphite lid and thermometer well in the graphite crucible containing the molten, metal freezing-point sample.



A. Silicone elastomer stopper.
B. Fused quartz tube.
C. Graphite thermometer well.
D. Tungsten rod sealed in fused quartz tube.
E. Graphite lid.
F. Induction heater coils.
G. Graphite crucible.
H. Metal sample.

Figure 8. Apparatus for inserting graphite thermometer well into the graphite crucible containing the molten metal sample. [The weighted fused-quartz tube slides the thermometer well through the hole in the lid into the molten metal. The mass of the weighted fused-quartz tube was designed to be greater than the buoyant force of the molten metal.]

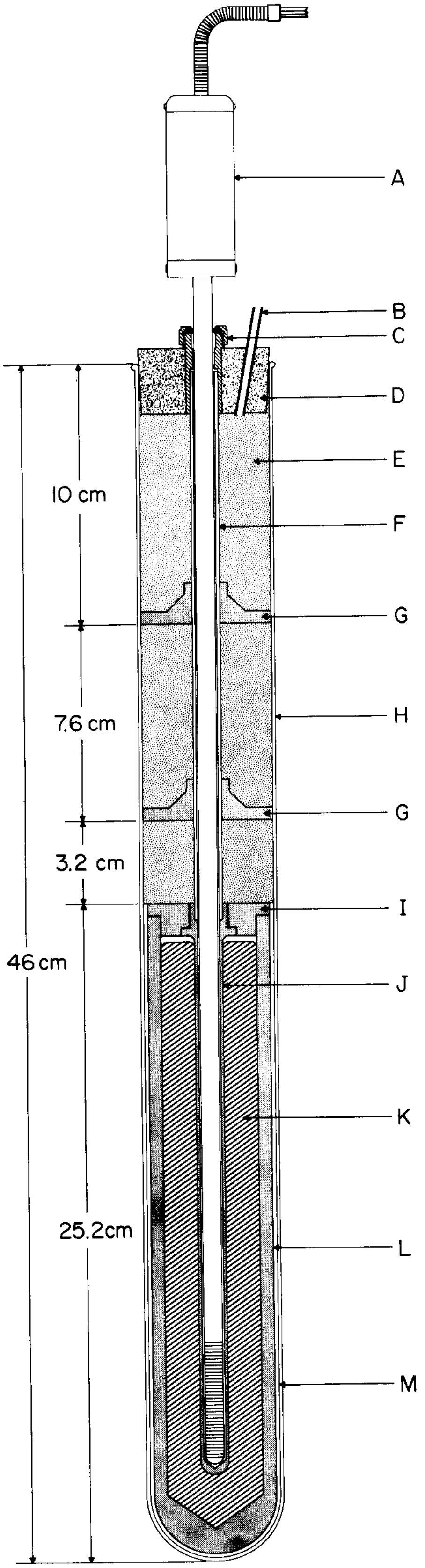
the filled graphite crucible. (This graphite cell design has been used with aluminum, cadmium, tin, and zinc samples). Before fitting the lid snugly into the top of the crucible, the thermometer well was tested to slide smoothly under its weight through the central hole in the lid. When the fit was too snug, the well was pushed through the hole several times to erode some of the graphite to loosen the fit. When the fit of the thermometer well and lid hole was suitable, they were assembled with the crucible and placed inside a fused-quartz tube as shown in Figure 8. [Since the assembly shown in Figure 8 was used also with aluminum, fused quartz was used instead of borosilicate glass.] A tungsten rod, that was sealed in a fused-quartz tube and then inserted into the thermometer well, added enough extra mass so that the well would sink into place when the metal was melted. With zinc about 0.3 atmosphere pressure of purified argon was admitted into the fused quartz tube space during the melting period to reduce the volatilization of the metal. The induction heating power was gradually increased until melting started as indicated by the sinking thermometer well. When the thermometer well sank to the proper position the induction heating power was turned off and the cell was allowed to cool.

2.4 Assembly of Freezing-Point Cells

The zinc sample, now completely enclosed in the graphite crucible with thermometer well and lid in place, was slipped into a precision-bore borosilicate glass tube (see Figure 4) for assembly into a zinc freezing-point cell as shown in Figure 9. A layer or two of Fiberfrax paper between the bottom and side of the graphite crucible and the borosilicate glass holder served as a cushion as well as thermal insulation during the freezing experiments. The cell assembly was designed to seal the stem of the SPRT and the contents of the glass tube in helium gas to provide an inert atmosphere for the zinc sample and graphite components and good thermal conductance to the SPRT. The cell was used with the helium-gas pressure slightly above ($\sim$ 250 Pa) the ambient pressure. The two graphite heat shunts (see Figure 6), indicated as G in Figure 9, were fitted closely to the inner wall of the glass cell H and the outer wall of the glass thermometer guide tube F. The shunts provided heat to the thermometer guide tube of the cell which in turn tempered the stem of the SPRT and increased the effective "immersion" of the SPRT. The outer section of the glass cell H where the two heat shunts were placed was ground to fit snugly a metal sleeve, which was in turn in good thermal contact with the top block of the furnace core so that the temperature of this section could be controlled by the furnace. (See Section 2.5 for the description of the furnace.)

2.5 Freezing-Point Furnace

The design of the furnace that was employed with the zinc freezing-point cell is shown schematically in Figure 10. The furnace was designed to provide a highly uniform and precise temperature control. The furnace core has a coaxially arranged stack of three aluminum cylinders [top



A. Platinum resistance thermometer.
B. To helium gas supply and pressure gauge.
C. Thermometer stem seal with silicone rubber.
D. Silicone rubber stopper.
E. Insulation, washed Fiberfrax.
F. Thermometer guide tube, borosilicate glass.
G. Heat shunt, graphite.
H. Borosilicate glass cell.
I. Graphite lid.
J. Graphite thermometer well.
K. Metal sample.
L. Graphite crucible.
M. Insulation, Fiberfrax paper.

Figure 9. Freezing-point cell of zinc, tin, or cadmium.

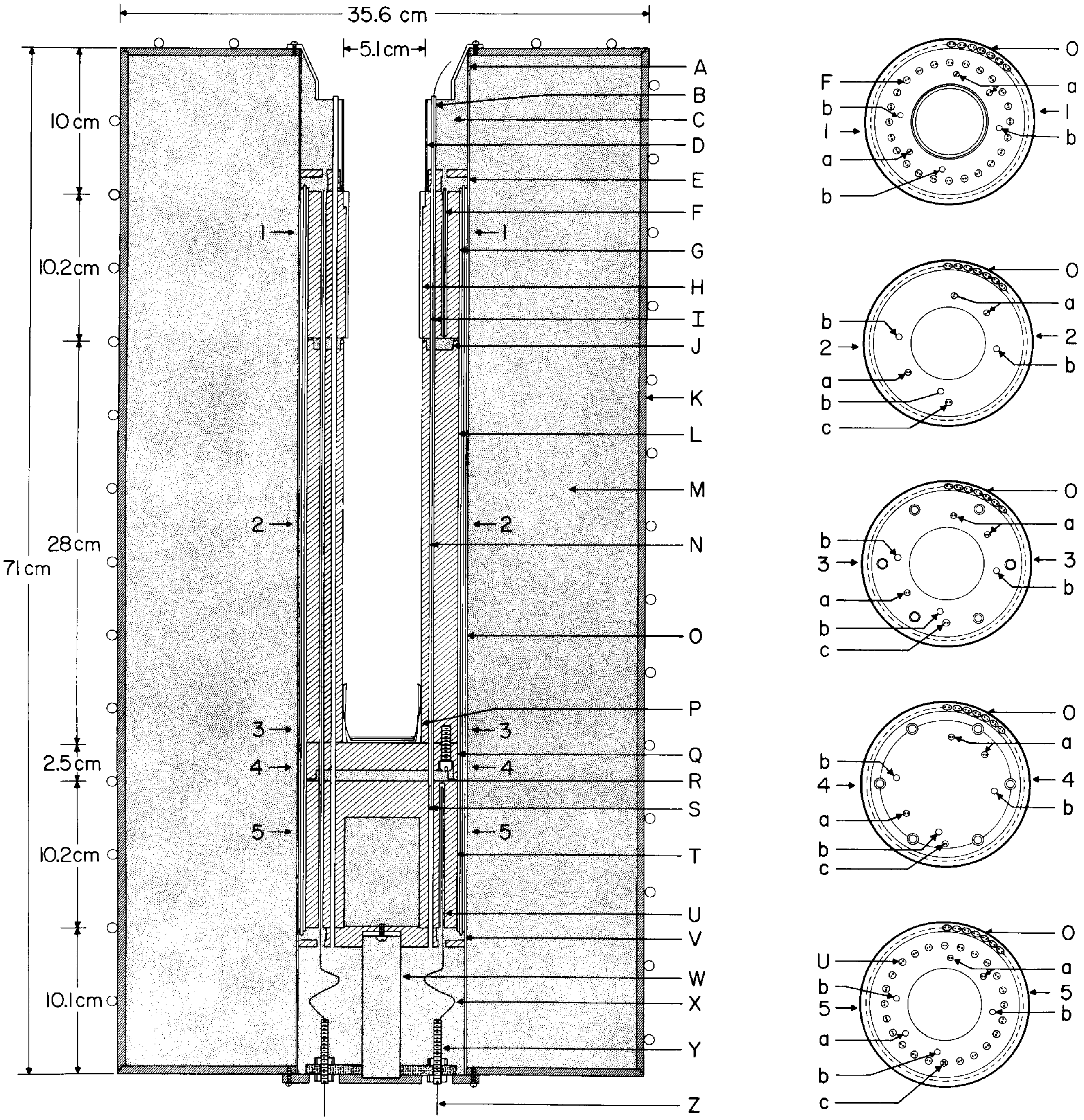


Figure 10. Schematic of furnace used with zinc- and tin-point cells. [In the investigation of the reproducibility of the cadmium point, that is described in this paper, the furnace shown in Fig. 22 was used; however, the furnace shown here can also be used with cadmium-point cells.]

Figure 10. Schematic of furnace used with zinc- and tin-point cells. [In the investigation of the reproducibility of the cadmium point, that is described in this paper, the furnace shown in Fig. 22 was used; however, the furnace shown here can also be used with cadmium-point cells.]

A. Stainless steel tube, 11.4 cm o.d. x 0.76 mm wall.
B. Stainless steel tubes (6); 3.20 mm o.d. x 0.013 mm wall.
C. Insulation, Fiberfrax mats.
D. Stainless steel tube.
E. Insulation, Fiberfrax mats and mica sheets.
F. Control heaters for top core block.
G. Top core block.
H. Sleeve (aluminum or Inconel) for metal freezing point cell.
I. Elevation of thermocouple junction (Chromel-P/Alumel), top core block. (See a).
J. Insulation, Fiberfrax sheets.
K. Brass shell, 4.8 mm thick.
L. Center core block.
M. Insulation, bulk Fiberfrax.
N. Elevation of thermocouple junction (Chromel-P/Alumel), center core block. (See a).
O. Main heaters, held on with Inconel "garters".
P. "Spider" for centering the freezing point cell.
Q. Center core block end plate.
R. Insulation, Fiberfrax sheets.
S. Elevation of thermocouple junction (Chromel-P/Alumel bottom core block. (See a).
T. Bottom core block.
U. Control heaters for bottom core block.
V. Insulation, Fiberfrax mats and mica sheets.
W. Stainless steel tube support, 2.5 cm o.d. x 0.51 mm wall x 11.4 cm long.
X. Heater leads.
Y. Posts for heater leads.
Z. To electric power.
a. Wells (B) for control thermocouples (See I, N, and S).
b. Wells (B) for testing the temperature profile of furnace core.
c. Leads from top core block heaters.

(G), center (L), and bottom (T)] which are thermally insulated from each other with Fiberfrax paper. A Nichrome V wire heater (main heater, O), installed inside two-hole oval alumina tubes, extends the full length of the three blocks. These alumina tubes are closely spaced around the length of the core and are held tightly against the blocks. The top and bottom blocks each have an additional heater constructed of Nichrome V wires (F and U) installed inside two-hole, round alumina tubes and inserted into holes drilled through the blocks. The entire core of the furnace, including the three blocks and the heaters, slips into a thin-wall stainless steel tube (A). The weight of the core rests on a thin-wall stainless steel tube (W). The space around the core is packed with Fiberfrax insulation.

The top block (G) was designed to receive either an aluminum or Inconel sleeve (H), that was bored to fit as closely as possible the glass freezing-point cell where the heat shunts are located (see Figure 9). [Since the NBS freezing-point cells have uniform outside diameters, a single sleeve fits all of them. However, the sleeve is removable from the furnace so that sleeves of other sizes could be used with cells of other laboratories with slightly different diameters.] After long continuous use at the zinc point the aluminum sleeve was found to bond to the aluminum top block; hence, for the last several years split Inconel sleeves have been employed exclusively with the furnaces.

The temperature of the center core (L) is controlled by means of an "absolute thermocouple" (N) and the main heater (O). The temperatures of the top (G) and bottom (T) blocks are controlled relative to the center block temperature by means of differential thermocouples [(I) and (S), respectively] and heaters [(F) and (U), respectively] in the blocks. The electric power to each of the heaters is controlled independently and automatically from the indication of the appropriate thermocouple. Tests on the uniformity of the furnace core showed that at 235°C the center core temperature was uniform ± 0.02°C [16].

Two furnaces of the above design were constructed for the NBS Platinum Resistance Thermometer Calibration Laboratory. For operating convenience, one is being used with zinc-point cells and the other with tin-point cells; however, they can be used interchangeably. Freezing-point cells of other metals (e.g., indium, cadmium, lead, or bismuth) with freezing points below that of aluminum can be used in the furnaces. Antimony-point cells (freezing point: 630.755°C) should be used with a copper-core furnace similar in design to the aluminum-point furnace described in Section 4.5 to avoid accidental melting of the aluminum furnace core by over-heating.

2.6 Preparation of Zinc-Point Freeze

Liquid zinc has been found to supercool about 0.02 to 0.06°C; hence, its freeze can be initiated in the furnace without withdrawing the zinc-point cell from the furnace. In contrast, with the tin-point cell where the liquid tin supercools as much as 25°C, the cell is withdrawn from the furnace to initiate the freeze (see Section 3.5).

The following is the procedure usually used in calibrating SPRT's at the zinc point.

1.) On the day prior to calibration of SPRT's, the furnace temperature control is set about 5°C above the zinc melting point and the sample is allowed to melt overnight. After the sample starts to melt, it is completely melted within about three hours at this temperature. Occassionally, the furnace temperature has been held as much as 20°C above the melting point to hasten the melting process. (At the NBS, the zinc and tin freezes are conducted in separate furnaces. When the cells are not being used, they are stored in the furnaces a few degrees below their respective freezing points. Whenever it is necessary to remove the cells from the furnaces, the cells are first cooled slowly in the furnace, by turning the furnace power off, to avoid possible breakage of the graphite crucible by too rapid cooling.)

2.) The following morning, after inserting a monitoring SPRT[4] into the cell, the furnace temperature control is reset to about 5°C below the freezing point, which results in cooling sufficiently rapidly to initiate the freeze spontaneously.

3.) About 5 minutes after the monitoring SPRT indicates that the recalescence associated with the initiation of the freeze has occurred, the SPRT is removed and two borosilicate-glass rods are inserted successively into the thermometer well for about 3 to 5 min each to induce an inner freeze immediately next to the thermometer well.

4.) During this time, the furnace temperature control is reset to 1° C below the freezing point.

5.) After withdrawing the second borosilicate-glass rod, the cold monitoring SPRT is inserted into the thermometer well and the equilibrium temperature is observed after about 45 min. Meanwhile, a test SPRT is preheated in an auxiliary tube furnace held at about 20°C above the zinc point.

6.) After completion of the measurements on the monitoring SPRT, it is removed from the zinc-point cell and the test SPRT is withdrawn from the preheating furnace and quickly inserted into the cell. The thermometer temperature, at the time of insertion into the cell

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[4] At the NBS, separate monitoring or check SPRT's are used with different metal fixed points and comparison calibration apparatus. They are used to test the consistency of the calibration process. Any deviation from the established results indicates immediately that the measurement process is not normal.

well, should preferably be slightly below that of the cell. (The SPRT is inserted slightly colder than the cell temperature to avoid melting and loosening of the solid zinc mantle around the thermometer well.) When the SPRT is preheated to a temperature close to that of the cell temperature, temperature equilibrium with the cell is attained within a few minutes after insertion (see Figure 11). Preheating of the SPRT also reduces the amount of metal frozen and, hence, permits more SPRT's to be calibrated in the same freeze.

7.) The resistance readings of the test SPRT are started about 15 min after inserting it into the zinc-point cell. Meanwhile, a second test SPRT is preheated in the auxiliary furnace.

8.) After completion of the measurements on the first test SPRT, it is replaced in the zinc-point cell by the second test SPRT. (Meanwhile, a third test SPRT is preheated in the auxiliary furnace. Usually a maximum of six test SPRT's are calibrated in any single zinc freeze).

9.) When the final test SPRT is inserted into the zinc-point cell, the monitoring SPRT is preheated in the auxiliary furnace.

10.) When the readings on the final test SPRT are completed, it is replaced in the zinc-point cell by the preheated monitoring SPRT. This second reading with the monitoring SPRT must not differ from the first reading by more than 0.5 mK. Usually the difference is not more than 0.1 or 0.2 mK. If the difference is larger than 0.5 mK, the measurements on some of the test SPRT's that were calibrated last will be repeated using another zinc freeze. The test SPRT's on which the measurements are to be repeated are selected on the basis of the elapsed time since the start of the freeze and the change in the freezing temperature that is observed with the monitoring SPRT.

When the zinc-point freeze is prepared as outlined above, freezes of 14 to 16 hours' duration are obtained. With cells assembled using SRM-740 zinc standard, the change observed in the freezing point while the first 50 percent is frozen is less than 0.2 mK. Figure 12 shows the results of continuous observation of the freezing temperature without disturbing the SPRT. In this particular freeze, two cold SPRT's were successively inserted into the thermometer well (instead of two cold glass rods) to induce the inner freeze of solid zinc mantle around the thermometer well. The freeze, with the furnace temperature at 0.9°C below the freezing point, lasted about 18 hours with maximum temperature change of about 1.7 mK. The freezing curve shows a temperature change of only 0.5 mK over the initial 75 percent of the freeze. (It is essential, before using the final assembled cells for calibration of SPRT's, to obtain first complete freezing curves to assess the purity of the metal and to assess the quality of the freezing points that can be obtained).

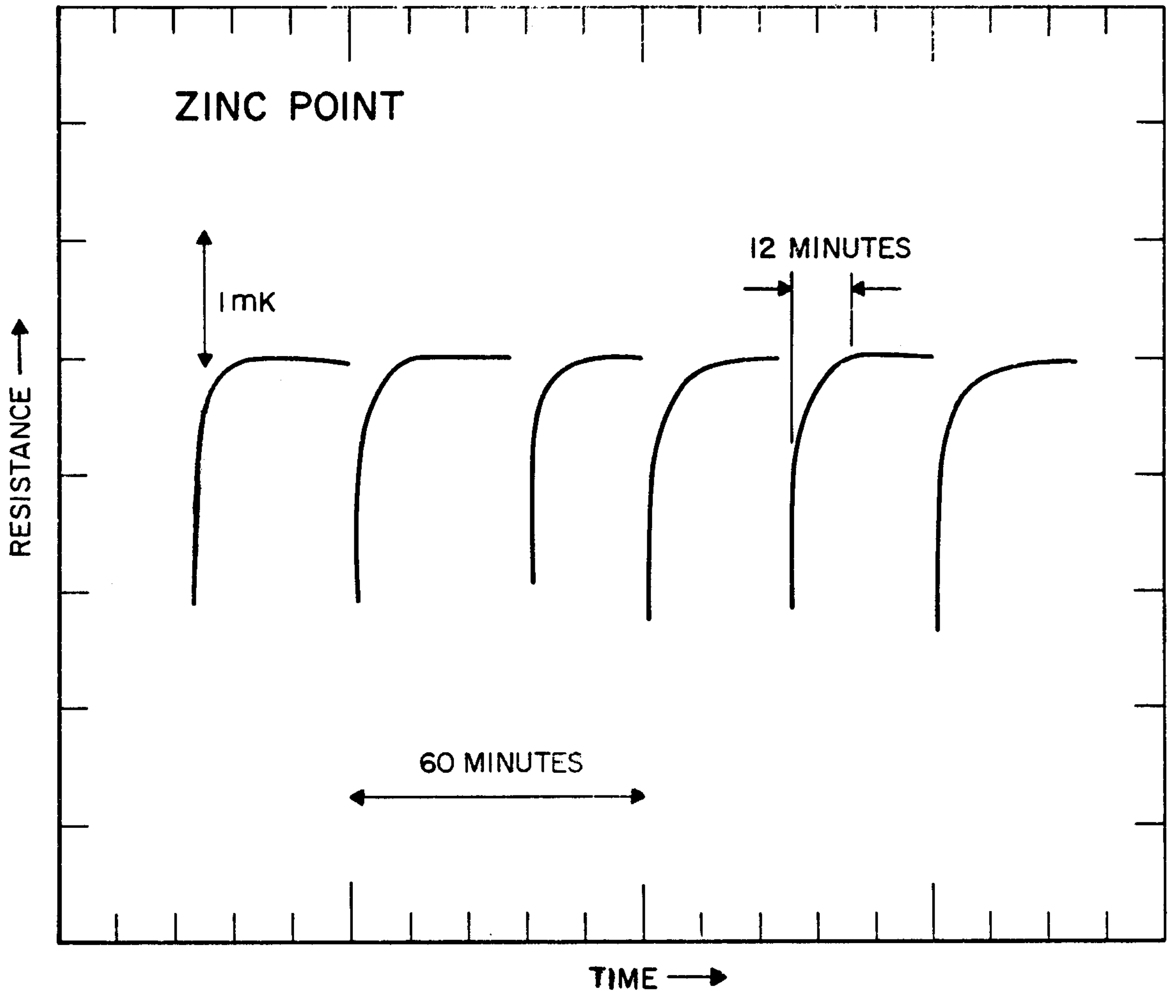

Figure 11. Consecutive measurements of the resistance of an SPRT in a single zinc freeze (SRM-740).

[An a-c bridge was employed in the measurements. Following each equilibrium resistance observation, the SPRT was completely withdrawn from the zinc-point cell, exposed to the ambient temperature for one minute, and reinserted into the cell. In the actual procedure employed in calibration the SPRT is preheated close to the zinc point (see text). The data show that the SPRT comes rapidly to equilibrium even when inserted into the cell relatively cold. For comparison when the SPRT was hotter than the cell temperature, see Fig. 14 (tin) and Fig. 31 (mercury).]

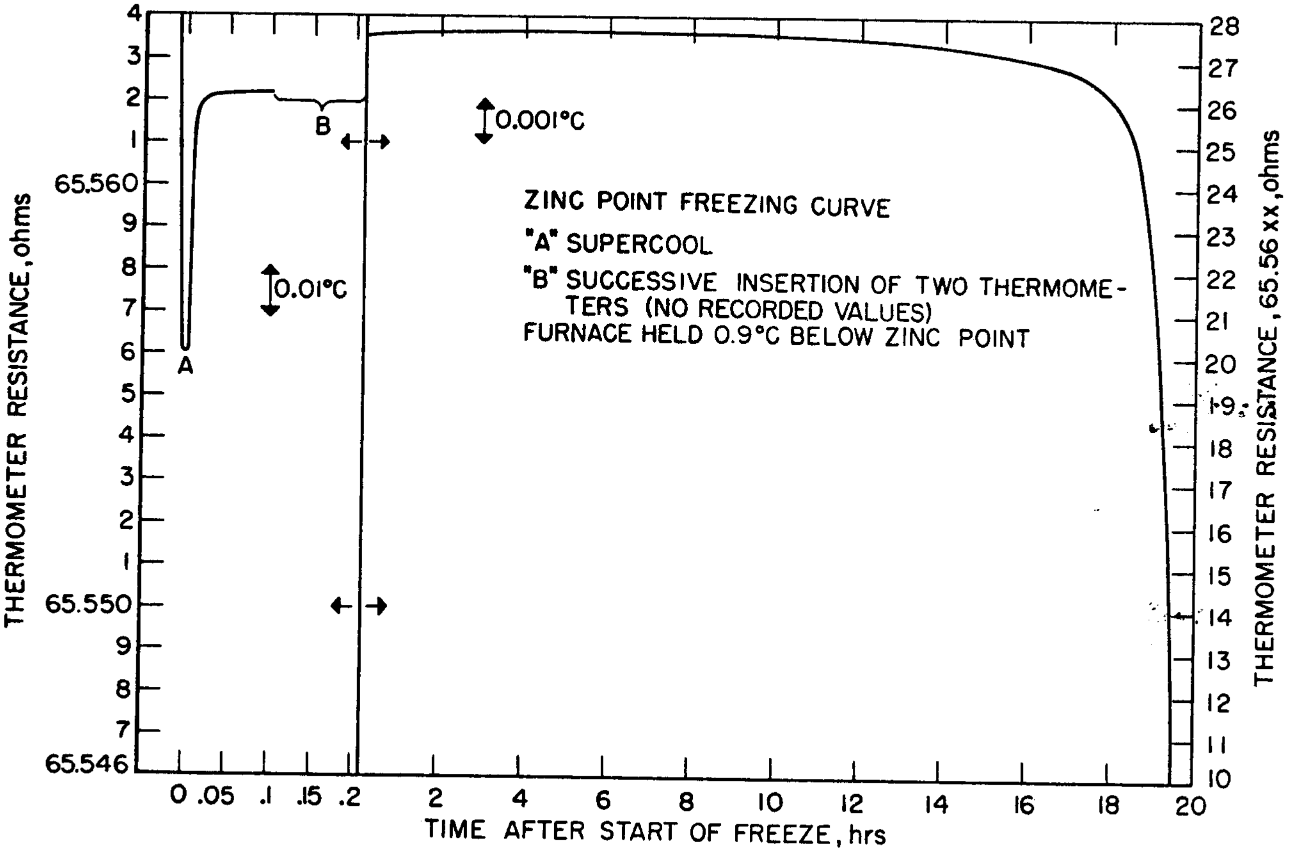

Figure 12. Freezing curve of zinc (SRM-740).
[The head of the SPRT was adapted for coaxial connectors and an a-c bridge was used. The furnace was controlled at 0.9 K below the zinc point. The mass of zinc sample was 1280 g. In this measurement, two cold SPRT's were inserted in the cell at "B" to freeze a coating of zinc around the graphite thermometer well.]

Different monitoring SPRT's are used with zinc and tin point cells. Measurements at the triple point of water are obtained for every measurement of the monitoring SPRT's at these metal freezing points. The accumulated results on the monitoring SPRT's give information on whether the present calibration process is consistent with the past measurements. At the NBS, monitoring or check SPRT's are used in both fixed-point calibrations and comparison calibrations of all SPRT's. Such measurements on the check SPRT's are part of the nucleus of measurements for measurement assurance in SPRT calibration at the NBS.

Figure 11 shows the results of consecutive measurements of an SPRT in the same zinc freeze. Following each equilibrium resistance observation, the SPRT was completely withdrawn from the zinc-point cell, exposed to the ambient temperature for one minute, and then reinserted into the cell. As described earlier, in the actual calibration procedure the SPRT is preheated close to the zinc point to achieve temperature equilibrium within the freezing point cell as quickly as possible. The results of Figure 11 show that the SPRT comes rapidly to equilibrium with the cell even when inserted relatively cold. (See also Figure 14 for equilibrium behavior when a preheated SPRT was inserted both hotter and colder than the tin-point temperature).

3. Tin Freezing Point

The state of thermodynamic equilibrium between solid and liquid tin at 1 standard atmosphere of pressure is assigned the value 231.9681°C (505.1181K), henceforth referred to as the freezing point of tin or, simply, the tin point; it is the specified alternative to the normal boiling point of water (steam point, 100°C) which is one of the fixed points used to define the IPTS-68. Prior to 1966 the steam point was maintained at the NBS for the calibration of SPRT's; however, since 1966 the tin point has been maintained instead. The tin point can be realized with greater reproducibility and ease than can the steam point.

3.1 Tin Samples

Two series of tin freezing-point standards, SRM-42g (lot HPM 6637) and SRM-741 (lot HPM 6779), are available.[5] SRM-42g tin samples are nominally 99.999 percent pure. They were prepared by electrolyzing (without addition agent) carefully selected commercially refined tin (99.97 percent pure), melting and homogenizing the electrolyzed product, and casting into semi-cylindrical bars 5 cm across the flat side and about 60 cm long.

SRM-741 tin samples are nominally 99.9999 percent pure. They were prepared by zone refining the electrolyzed product by at least twenty zone passes. The zone refined product was melted and homogenized and then cast into semi-cylindrical bars similar in size and shape to SRM-42g. (At the NBS, only SRM-741 tin is used in the calibration of SPRT's.)

Assay certificates that accompanied the lot HPM 6779 and 6637 samples from the supplier listed the impurities given in Table VIII. The analysis indicates that the concentration of Pb was significantly reduced in SRM-741 by zone refining. The assay was based on spectrochemical analysis of a "master" sample from each lot. Also, samples taken from the ends of two selected bars each from the two SRM's were analyzed spectrochemically in the Spectrochemical Analysis Section of the NBS and in the laboratory of the supplier. The results are summarized in Table IX.

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[5] The SRM-42g samples were made from tin bars of lot HPM 6637; these references to the material will be used interchangeably. Similarly, the SRM-741 samples were made from tin bars of lot HPM 6779; these references to the material will also be used interchangeably. The NBS-OSRM obtained from the supplier three lots of tin of about 159 kg each. Two of the lots, designated by the supplier HPM 6637 and 7039, are nominally 99.999 percent purity; the third lot, designated HPM 6779, is nominally 99.9999 percent pure (NBS Order No. S-45045-67, Contract No. CST-309).

Table VIII

Emission Spectrochemical Analysis of the Tin Samples

(From the Assay Certificates of Supplier)

	Supplier	
Element	SRM-741[a] Lot HPM 6779 (in ppm)	SRM-42g[b] Lot HPM 6637 (in ppm)
In	0.1	0.2
Mg	<0.1	<0.1
Pb	0.2	1.
Si	<0.1	0.1
Cu		0.1

[a] Date: December 23, 1966

[b] Date: October 19, 1966

Table IX

Emission Spectrochemical Analysis of the Tin Samples[a]

Element	SRM-741 (Lot HPM 6779) Specimen				SRM-42g (Lot HPM 6637) Specimen			
	1A	1B (in ppm)	35A	35B	1A	1B (in ppm)	35A	35B
Ag	<1	<1	<10	<1	<1	<1	<1	<1
Al	?				?			
Ca	?	<1	<1	<1	?	<1	<1	?
Cu	<1	?	<1		<1	?	<1	<1
Fe	?	<1	<1	<1	<1	<1	<1	<1
Mg	<1	<10	<10	<1	<1	<1	<10	<1
Ni		<1	?	?	<1	?	<1	
Pb					?			
Pt			?					
Si	<10	<10	<10	<10	<10	<10	<10	<10

[a] Analysis of millings of each sample by a general qualitative spectrochemical method by Elizabeth K. Hubbard, Spectrochemical Analysis Section, National Bureau of Standards (May 16, 1967).

(contd.)

Table IX
(continuation)

Emission Spectrochemical Analysis of the Tin Samples

	SRM-741 (Lot HPM 6779) Specimen				SRM-42g (Lot HPM 6637) Specimen			
Element	1A	1B	35A	35B	1A	1B	35A	35B
<u>Analysis by the supplier</u> (December 4, 1967)								
Ag					<0.1	<0.1	<0.1	<0.1
Ca					ND	ND	ND	ND
Cu					ND	0.1	0.1	ND
In	ND[b]	0.1	0.1	0.1	0.5	0.5	0.5	0.5
Mg	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
Po	ND	0.1	0.1	0.1	1.0	1.0	1.0	0.7
Si	0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1	0.1

[b] ND = not detected.

The analyses of the two laboratories are in general consistent except for In and Pb. The analysis by the supplier indicated 0.2 and 1 ppm of In and Pb, respectively, in samples from lot HPM 6637 and 0.1 and 0.2 ppm of In and Pb, respectively, in samples from lot HPM 6779. The general qualitative emission spectrochemical analysis method employed at the time at the NBS did not detect these elements; special methods are probably employed in the laboratory of the supplier to analyze for them.

The results of mass spectrochemical analysis, summarized in Table X, show that Pb, As, Cu, and S are definitely present in samples from lot HPM 6779. The analysis on In and Pb is in agreement with the emission spectrochemical analysis reported by the supplier. The large amount of sulfur that was detected precludes the possibility that the tin samples of lot HPM 6779 are 99.9999 percent pure. However, the sulfur is expected to have insignificant effect on the freezing point. The high value (70 ppm) for silicon is an upper limit; emission spectrochemical analyses (see Tables VIII and IX) indicate 0.1 ppm or less. The silicon is probably present as silica and, as such, will not affect the freezing point.

Table XI summarizes the results of neutron activation analysis of two samples each from lots HPM 6637 and 6779. The analyses on In, La, and Cu are consistent with the results of both emission and mass spectrochemical analyses. Arsenic was detected in samples of both lots but was not determined quantitatively in the analysis.

The bars were received from the supplier individually sealed in argon-filled polyethylene bags. The bars were identified by numbers and the two ends were identified by A and B. Although efforts were made to produce bars of uniform composition within each SRM standard, the RRR measurements indicate that some segregation of impurities did occur, i.e., that the bars are not the same in purity nor completely homogeneous from one end to the other.

Deason *et al.* [8] (at the time with the Cryogenic Properties of Solids Section of the NBS at Boulder, Colorado) investigated the RRR of cylindrical samples of about 11 mm diameter and 30 mm length machined from each end of all of the tin sample bars from the supplier. Before making the measurements, the specimens were heavily etched removing about 0.26 mm from the diameter, washed, annealed at 200°C ± 15°C for one hour in a vacuum, and slowly cooled. Wide variations in the RRR between the paired ends of any single bar and among the bars were reported. The range of RRR of the thirty-one bars of lot HPM 6637 was from 17,700 to 26,400, while the variations in the RRR between the paired ends of any single bar ranged from essentially zero to 6900. The range of the RRR values of the thirty-two bars of lot HPM 6779 was somewhat larger, from 24,500 to 43,500, while the variations in the RRR between the paired ends ranged from essentially zero to 13,000. The data indicate that the impurities that affect the RRR are not uniformly distributed in both lots of tin samples. To determine whether the RRR values may be useful for selecting bars that would be suitable for freezing-point application, samples were selected to represent a wide range of RRR values from bars on which the RRR values of the two ends were the closest.

Table X

Mass Spectrochemical Analysis of the Tin Samples from SRM-741 (Lot HPM 6779)

Element	Specimen[a] 22B (in ppm)	 26A (in ppm)
S	28	13
Cu	0.1	0.07
As	0.06	0.04
Pb	0.3	0.5

Sn interfered with the following elements; the values are estimated upper limits

Element	PPM	Element	PPM
C	0.3	V	0.01
N	0.04	Cr	0.1
O	2	Mn	0.05
F	0.6	Fe	0.1
Na	2	Zr	0.06
Mg	0.05	Nb	0.2
Al	0.06	In	0.3
Si	70	Sb	0.5
Cl	0.2	Cs	0.2
K	0.4	La	0.1
Ca	2	Au	0.7

There was complete interference with P, Co, and Ni.

(contd.)

Table X (continuation)

The following values are the upper limits of elements not detected;

Element	PPM	Element	PPM	Element	PPM
Li	0.01	Ru	0.04	Ho	0.03
Be	0.01	Rh	0.01	Er	0.08
B	0.01	Pd	0.05	Tm	0.03
Ne	0.01	Ag	0.03	Yb	0.09
Ar	0.01	Cd	0.05	Lu	0.03
Sc	0.01	Te	0.05	Hf	0.08
Ti	0.01	I	0.02	Ta	0.03
Zn	0.01	Xe	0.06	W	0.10
Ga	0.01	Ba	0.03	Re	0.05
Ge	0.02	Ce	0.02	Os	0.08
Se	0.02	Pr	0.02	Ir	0.05
Br	0.02	Nd	0.07	Pt	0.10
Kr	0.02	Pm	0.02	Hg	0.10
Rb	0.01	Sm	0.08	Te	0.05
Sr	0.01	Eu	0.04	Bi	0.04
Y	0.01	Gd	0.10	U	0.04
Mo	0.05	Tb	0.02		
Tc	0.01	Dy	0.09		

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[a] The specimens were first etched in hydrocholoric acid solution and then washed in distilled water prior to sparking. The samples were presparked to identify and remove any surface contamination. The analysis was performed by C.W. Mueller and P.J. Paulsen, Analytical Chemistry Division, National Bureau of Standards (December 31, 1968).

Table XI

Neutron Activation Analysis of the Tin Samples

	SRM-741 (Lot HPM 6779) Specimen		SRM-42g (Lot HPM 6637) Specimen	
Element	26A	22B	19A	2B
		(in ppm)		
In	0.094±0.048[a]	0.126±0.016[a]	0.302±0.009[a]	0.317±0.031[a]
La	$1.05 \pm 0.46\mathrm{x}10^{3}$	$0.62 \pm 0.51\mathrm{x}10^{-3}$	$1.53 \pm 0.35\mathrm{x}10^{-3}$	$0.88 \pm 0.25\mathrm{x}10^{-3}$
Cu	0.036±0.13	0.057±0.021	0.34 ±0.27	0.102±0.060
As	Detected but not determined.			

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[a] Figures after the ± symbol indicate standard deviation. Analysis by H.L. Rook, Analytical Chemistry Division, National Bureau of Standards (August 5, 1970).

The samples that were selected, the designation of the tin-point cells that were prepared from the samples, and the corresponding RRR values are listed in Table XII. Since a sample for freezing-point measurements required a 20 cm segment of the 60 cm long bar, the "duplicate sample" from the same bar was from the middle of the bar. The value of RRR of the second sample was taken to be the mean of the two end values.

The results of the freezing-point measurements (see Figure 13) appear to be relatively insensitive to the variations of "impurities" that affect the RRR value. (See Section 3.6 for the description of freezing-point measurements.) In the region where the RRR values of tin samples from lots HPM 6637 and 6779 nearly overlap, the freezing points of the samples from the two lots are distinctly different, indicating that the "impurities" that affect the RRR values are different from those that affect the freezing point.

3.2 Graphite Cells for Tin

At the time the tin-point cells were assembled the graphite thermometer well-lid assembly with screw threads shown in Figure 2 was used with the crucible of Figure 1. The simpler thermometer well-lid assembly of Figure 3 is expected to be used for the assembly of future tin-point cells.

3.3 Filling Graphite Cells with Tin

The same equipment arrangement (Figure 5) used to fill graphite crucible with zinc was used with the tin samples. Since tin at its melting point has very low vapor pressure, the bell jar was evacuated to 0.01 torr (1 torr = 1 mm Hg, 0°C = 133.322 Pa [37]) or lower pressure by a mechanical pump that was "trapped" with molecular sieve. (The vapor pressure of tin at its melting point is estimated to be about 6×10^{-21} Pa [28].) The funnel containing the tin sample and the graphite crucible were heated inductively to a temperature a few degrees below the tin point while pumping. After about 1 hour, the induction heater power was increased to melt the tin sample into the crucible. It required about 15 minutes to melt the sample completely. The sample was then allowed to cool nearly to room temperature. The bell jar was filled to atmospheric pressure with argon gas and the graphite crucible containing the solidified tin was transferred into the same borosilicate glass tube (shown in Figure 7) used with zinc for inserting the thermometer well-lid assembly. The procedure used for inserting the thermometer well-lid assembly was the same as described for zinc (see Section 2.3).

3.4 Tin Freezing-Point Cells

The tin-point cells were assembled by installing the graphite cells containing tin samples inside borosilicate glass tubes. The assembly procedures and the dimensions of the completed cell were the same as those of zinc cells (see Section 2.4 for details). As mentioned earlier, the cell dimensions have been standardized so that the cells and furnaces could be interchanged.

Table XII

Identification of Tin Samples by Bar Number, Residual Resistivity Ratios, and Designation of Assembled Tin-Point Cells

PRT-LAB Cell Designation	Sample	RRR[e] Bar End A	RRR[e] Bar End B
	(SRM-741, Lot HPM 6779)		
C	34B	36,379	40,948
E	29A	36,030	36,060
G	7B	32,993	32,048
H	8B	28,571	27,778
I	23A	41,800	32,487
J	33A	40,504	31,491
K[a]	26A	43,456	30,419
L[b]	25A	38,642	33,351
M[c]	30B	36,436	39,711
N	30[d]	36,436	39,711
O	23[d]	41,800	32,487
P	33[d]	40,504	31,491
Q	26[d]	43,456	30,419
	(SRM-42g, Lot HPM 6637)		
B	13B	19,423	18,520
D	10B	21,855	21,935
F	25A	25,042	22,757
	(LAB STD)		
LAB STD (LS)		No RRR measurements	

[a] Thermometer well broke after measurements.

[b] Thermometer well broke before any measurements could be made.

[c] Accidentally overheated to above 500°C before any measurements were made.

[d] These are second samples from the same bar. The RRR values assigned to these samples are the mean of the values of the two ends of the bar.

[e] Measurements by V.A. Deason, A.F. Clark, and R.L. Powell [8].

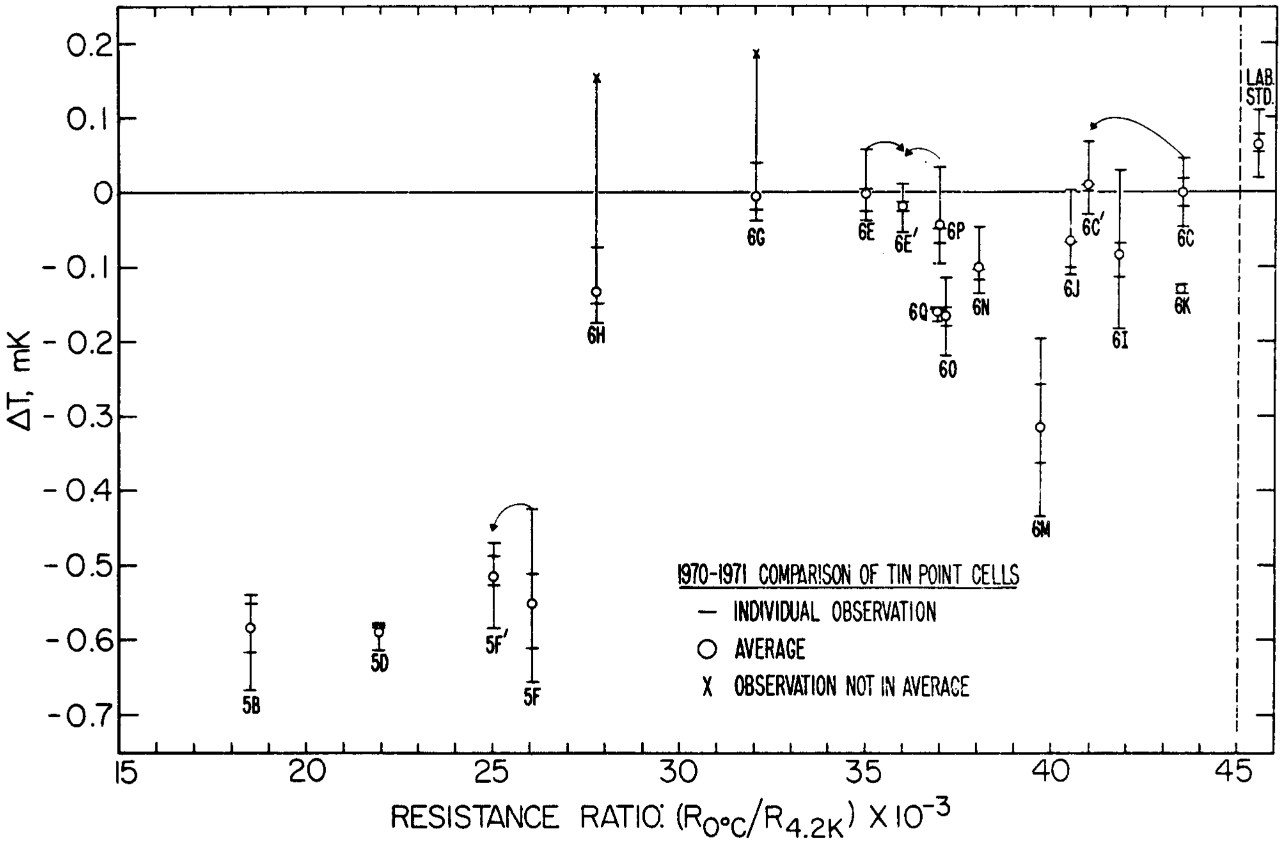

Figure 13. Comparison of tin freezing-point temperatures with different residual resistance ratios: R(0°C)/R(4.2K).

[The prefixes 5 and 6 indicate samples nominally 99.999 percent pure (SRM-42g, Lot HPM 6637) and samples nominally 99.9999 percent pure (SRM-746, Lot HPM 6779), respectively. The alphabetic character identified the cell. The prime (') identifies a second set of measurements of the same cell. LAB. STD. is a tin-point cell that has been used at the NBS in the calibration of SPRT's. Observations from four separate freezes are shown for each cell. The plateau temperature selected was the reading 1.5 hours after the initiation of the freeze; the temperature corresponded to about 25 percent frozen. The temperatures of the SPRT during the previous hour differed typically 0.02 or 0.03 mK but not more than 0.1 mK from the selected temperatures of any measurements. The observed plateau temperatures are shown relative to the mean value obtained for the tin-point cells 6C and 6E. Cell 6M was accidentally overheated above 500°C before the measurements. Only two measurements were obtained for cell 6K.]

3.5 Freezing-Point Furnace for Tin

For the description of the furnace used for melting and for obtaining the tin freezing point, see Section 2.5. The furnaces used with the zinc and tin cells have the same design; however, the procedures used to obtain their freezes are different.

3.6 Preparation of Tin-Point Freeze

Liquid tin has been found to supercool as much as 25°C. The degree of supercool depends upon the temperature and length of time the metal has been allowed to remain melted and upon the rate the liquid metal is cooled. Impurities (e.g., Fe) seem to reduce the degree of supercool [5]. If the freeze were initiated by lowering the furnace temperature with the tin-point cell in the furnace, the furnace block temperature could not be returned to the freezing-point temperature fast enough to avoid excessive freezing of the tin. Hence, the tin freeze is initiated by employing the "outside nucleated" freeze technique described earlier by McLaren and Murdock [26].

The procedure usually used in preparing the tin-point freeze for calibrating SPRT's is as follows. (The description follows the procedure used with SRM-741 tin-point cells; the same procedure could be used with the less pure SRM-42g tin-point cell.)

1.) The tin sample is melted overnight in the furnace held at a temperature about 3°C above the melting point. After the sample starts to melt, it is completely melted within about five hours at this temperature.

2.) In the morning, a monitoring SPRT is inserted into the thermometer well and the furnace control is reset down to a temperature 1°C below the freezing point. (The monitoring SPRT used with the tin-point cell is different from that used with the zinc-point cell).

3.) When the monitoring SPRT indicates that the tin sample has cooled to near the freezing point, the cell is withdrawn from the furnace and held out in room temperature where rapid cooling and the start of freezing occurs (whence the term "outside nucleated" freeze). When the monitoring SPRT indicates that recalecence has started, the cell is quickly reinserted into the furnace.

4.) The equilibrium temperature resistance of the monitoring SPRT is usually obtained approximately 45 min after reinserting the tin-point cell into the furnace. The comparison of measurements with induced inner freeze around the thermometer well with those measurements prior to inducing the inner freeze has been found to be within 0.1 mK. [The inner freeze around the thermometer well is induced by inserting successively two cold borosilicate-glass rods into the well as described in Section 2.6]. Hence, the SPRT calibration is usually performed without the inner freeze.

5.) While the tin-point cell and the monitoring SPRT are equilibrating, a test SPRT is preheated in an auxiliary furnace held about 20°C above the tin-point.

6.) When the measurements on the monitoring SPRT are completed, it is removed from the tin-point cell and the test SPRT is withdrawn from the preheating furnace and quickly inserted into the cell so that the thermometer temperature during the insertion is approximately that of the cell. [In actual practice, unless the thermometer resistance is continuously observed, it is not known whether any melting or any additional freezing occurs upon insertion of the SPRT. In either event the preheated SPRT reaches temperature equilibrium with the cell within a few minutes (see Figure 14).]

7.) The resistance readings of the test SPRT are started 15 min. after inserting it into the tin-point cell. Meanwhile, a second test SPRT is preheated in the auxiliary furnace. The preheating and resistance measurement procedure with test SPRT's is very similar to that used with the zinc-point cell. As with the zinc-point cell, usually a maximum of six test SPRT's are calibrated in any single tin freeze.

8.) When the final test SPRT is inserted into the tin-point cell, the monitoring SPRT is preheated in the auxiliary furnace.

9.) After the readings on the final test SPRT are completed, it is replaced in the tin-point cell by the preheated monitoring SPRT. As in the measurements of the monitoring SPRT used with the zinc-point cell, this second reading of the monitoring SPRT used with the tin-point cell must not differ from the first reading by more than 0.5 mK. Usually the difference is not more than 0.1 or 0.2 mK. If the difference is larger than 0.5 mK, the measurements on some of the test SPRT's that were calibrated last will be repeated next day using another tin freeze. The test SPRT's on which the measurements are to be repeated are selected on the basis of the elapsed time since the start of the freeze and the difference in the freezing temperatures that is observed with the monitoring SPRT.

When the tin-point freeze is prepared as described above, freezes of 12 to 14 hours' duration are obtained. The duration of the freeze depends upon the amount to which the tin sample supercooled before the freeze was initiated (see Section 3.6). With cells containing SRM-741

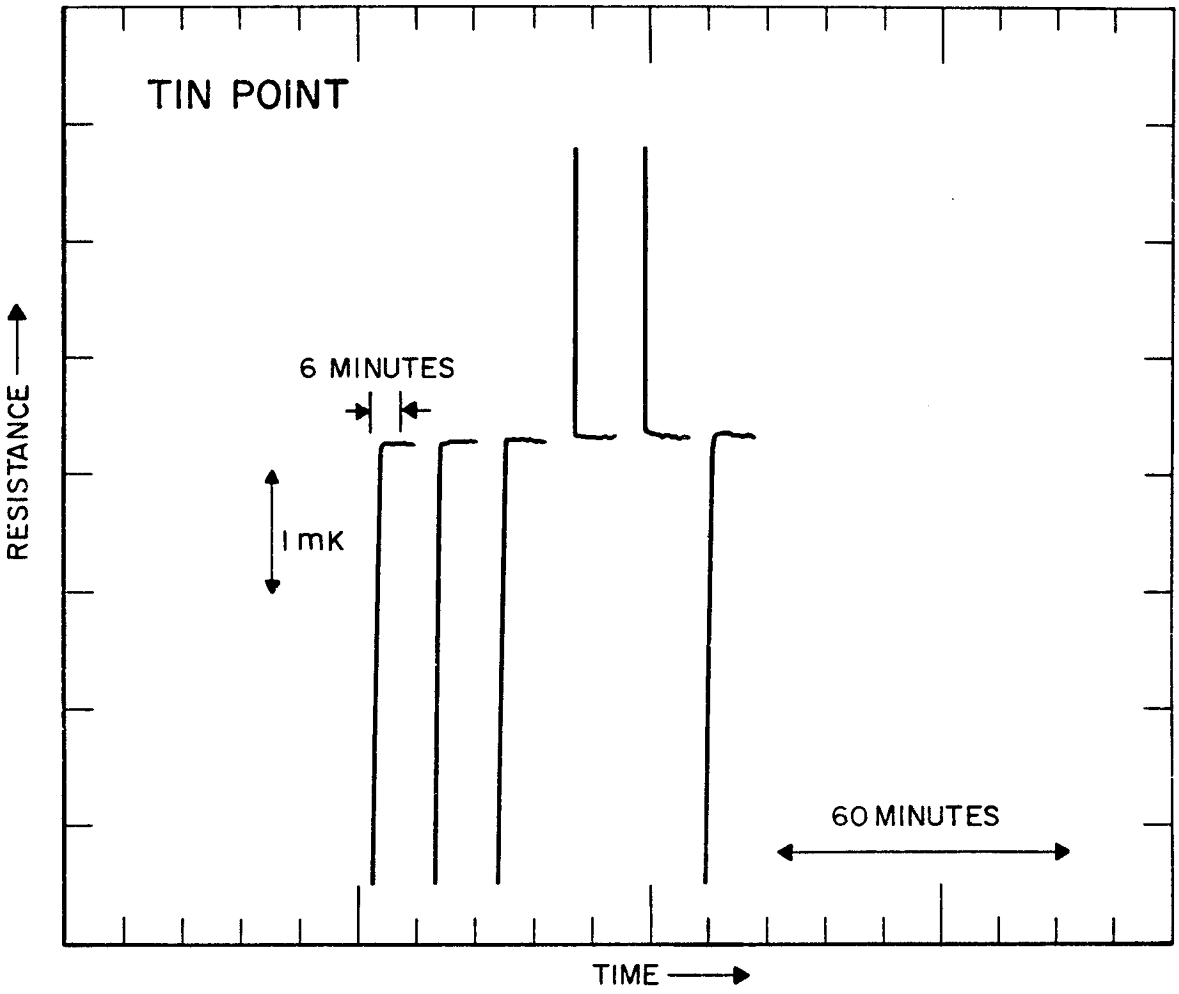

Figure 14. Consecutive measurements of the resistance of an SPRT in a single tin freeze (SRM-741).

[An a-c bridge was employed in the measurements. Following each equilibruim resistance observation, the SPRT was completely withdrawn from the tin-point cell, preheated close to the tin point in an auxiliary furnace, and reinserted into the cell. The data show that the preheated SPRT comes to equilibrium in a very short time. In two of the cases shown, the temperature of the SPRT when inserted into the cell was slightly hotter than the tin point. For comparison when the SPRT was not preheated close to the cell temperature, see Fig. 11].

tin standards, after the initial 5 percent of the freeze has occurred, the temperature change during the following 50 percent of the freeze is less than 0.2 mK. Figure 15 shows the results of continuous observation of the freezing temperature. The SPRT remained continuously in the cell from the very beginning of the freezing process. No inner freeze of solid tin was induced by inserting cold glass rods into the tin-point cell. The freeze, with the furnace temperature controlled 1°C below the freezing point, lasted about 15 hours with less than 1.4 mK total change in temperature. The freezing curve shows a temperature change of only 0.5 mK while over the initial 75 percent of the freeze similar to the SRM-740 zinc standard.

Figure 14 shows the results of consecutive measurements of an SPRT in the same tin freeze. Following each equilibrium resistance observation, the SPRT was completely withdrawn from the tin-point cell, preheated in an auxiliary furnace maintained at a temperature 20°C above the tin point, and reinserted into the cell. The results show that the preheated SPRT attains temperature equilibrium in a very short time. In two of the cases shown, the temperature of the SPRT when inserted into the cell was slightly above the tin-point temperature. (See Figure 11 where the SPRT was inserted into the zinc-point cell relatively cold.)

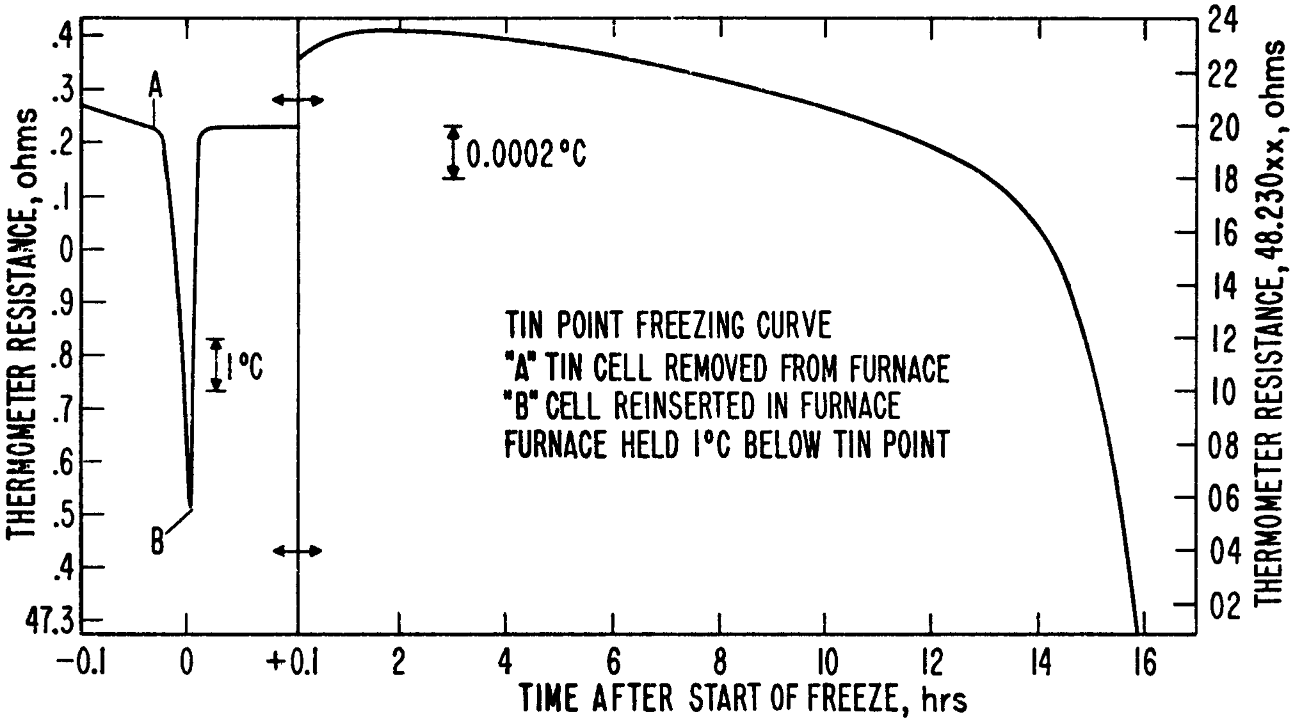

Figure 15. The freezing-curve of tin (SRM 741). [The head of the SPRT was adapted for coaxial connectors and an a-c bridge was used. The furnace was controlled at 0.9 K below the tin point. The mass of tin sample was 1300 g.]

4. Aluminum Freezing Point

The freezing point of aluminum, a secondary reference point with an assigned value of 660.46°C (933.61K) on the IPTS-68, has been used for many years in calibrating thermocouples [32]. In recent experimental investigations [13,24] the aluminum point has been shown to be highly reproducible (within ± 0.5 mK). Moreover, the aluminum point has also been suggested as one of the defining fixed points of the future international SPRT temperature scale [14].

The freezing point of antimony (630.755°C), another secondary reference point, is close to the freezing point of aluminum and has also been used for many years in calibrating thermocouples. However, the aluminum point has many advantages over the antimony point. Aluminum is much more abundant than antimony and, because of the greater technological importance of aluminum, it is available in greater amounts at high purity and at lower cost. At the freezing point, the vapor pressure of aluminum is about 2.5×10^{-6} Pa; on the other hand, that of antimony is about 26 Pa [28]. Also, aluminum is less toxic than antimony. The thermal diffusivity of liquid and solid aluminum at its freezing point was estimated to be many times greater than the corresponding values of liquid and solid antimony [2,15,17,30]. Liquid aluminum supercools 1 or 2°C while liquid antimony can supercool more than 20°C [24]. Hence, the realization of the freezing point of aluminum is simpler than that of antimony.

4.1 Aluminum Samples

Chemical analyses of aluminum bars as originally received from the supplier showed them to be of high purity; however, due to their poor general appearance they were indeed not suitable for distribution as SRM aluminum of high purity. Graphite particles were embedded in the aluminum bars of one lot, while numerous voids were scattered through the bars of another lot. The bars were subsequently recast to remove the above imperfections. However, before recasting, freezing-point investigations were made on samples from the original bars to test their suitability as freezing-point standards. The procedures that are described in this paper for assembling the freezing-point cells and for carrying out the freezing-point measurements were those followed on the original samples. The procedures are equally applicable to the recast samples. At this writing, freezing-point cells have been assembled using the recast aluminum samples; however, freezing-point measurements are yet to be made on them.

The original aluminum samples were received from the supplier in two lots in the form of cylindrical bars about 91 cm long. The bars of lot EM 1558 were 3.2 cm diameter, while the bars of lot EM 2571 were 3.8 cm diameter. Both lots had been purified by zone refining techniques and homogenized by melting together the various zone refined units. Bars of lot EM 1558 were made by casting in graphite molds, while those of lot EM 2571 were made by casting in alumina molds. The bars of lot

EM 1558 contained specks of graphite; the bars of lot EM 2571 contained a number of voids. The information supplied with lot EM 2571 suggests that the voids were caused by hydrogen that was dissolved in the liquid aluminum which on solidification expelled the hydrogen.[6]

The chemical analyses given in the assay certificates that accompanied the samples from the supplier are summarized in Table XIII. The assay is based on emission spectrochemical analysis. Except for Fe, the analyses of the supplier for the two lots of aluminum are about the same. The mass spectrometric analysis of lots EM 2571 obtained at the NBS, summarized also in Table XIII, shows that Fe and Zn are present in relatively high concentrations. The emission spectrochemical analysis apparently also did not detect the 0.2 ppm of Na that was detected in the aluminum by the mass spectrometric analysis. The limits of detection by the mass spectrometric analysis of some of the elements are listed in Table XIII.

If the worst case is considered, the analysis given in Table XIII indicates that the aluminum of lots EM 2571 could be about 99.9993 percent pure. The available analysis on lot EM 1558 indicates the material to be 99.9998 percent pure; however, the analysis on lot EM 1558 is not as extensive as that on lot EM 2571.

M.B. Kasen of the Cryogenics Division of the NBS at Boulder, Colorado, made RRR measurements of samples taken from the ends, middle, between middle and end, and outer surfaces of the aluminum bars of lot EM 2571 [20]. Of the total of 45 specimens (taken from 17 bars) that were examined, only two specimens were not within the RRR values of 5000 ± 250. The RRR values of the two exceptions were low (4670), these specimens being taken from the outer surface at the ends of a bar. They also had high surface porosity. The RRR measurements indicate that the aluminum sample bars of lot EM 2571 are fairly uniform. The "ultra-purity aluminum" samples (SRM-RM-1R and SRM-RM-1C, see sample certificate Appendix G) have the RRR values of about 16,200 or 16,600 [21], which suggests that the aluminum of lot EM 2571 could be of lower purity.

For freezing-point investigations the presence of graphite particles or voids in the original sample bars have very little influence on the results. Reference to freezing-point measurements or results in this paper are on specimens taken from the original aluminum bars of lots EM 1558 and EM 2571.

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[6] The solubility of hydrogen at 1 atm pressure in aluminum at the freezing point is about 0.5 to 0.8 cm^3 per 100 g of the liquid and about 0.04 to 0.05 cm^3 per 100 g of the solid [2]. The solubility of hydrogen in solid aluminum is apparently less at the lower temperatures, the reported solubilities at 400 °C being about 0.003 to 0.004 cm^3 per 100 g [2]. (The above volumes of hydrogen are in terms of the gas at 1 atm pressure and 20°C).

Table XIII

Chemical Analyses of the Aluminum Samples

Element	Lot EM 1558	Lot EM 2571	
	Supplier (in ppm)[a]	Supplier (in ppm)[b]	NBS (in ppm)[c]
Ca	0.2	0.2	
Fe	0.5	0.1	1.4
Mg	<0.1	0.1	0.2
Mn	0.1	0.2	≤0.3[c]
Si	0.3	0.3	
Cr	0.2		≤0.04
Cu	0.2	0.1	≤0.1
Ni			≤0.2
Ti			≤0.05
V			≤0.04
Na			0.2
Ga			≤0.06
Zn			5

[a] Based on spectrochemical analysis (August 30, 1971).

[b] Based on spectrochemical analysis (June 30, 1972).

[c] Mass spectrometric analysis by P.J. Paulsen, Analytical Mass Spectrometry Section, National Bureau of Standards (September 7, 1972).

[d] The values preceded by the symbol ≤ indicate the upper limit of the elements not detected.

The aluminum sample bars from lots EM 1558 and EM 2571 have subsequently been recast, in presence of chlorine, in fused quartz molds into thirty cylindrical bars of 3.8 cm diameter and about 46 cm length, the lot weighing about 50 kg total. The bars are now free of graphite particles and large voids. J.G. Hust (Thermophysical Properties Division, National Bureau of Standards) determined the RRR of the recast aluminum by the eddy current decay method in three different specimen sizes (approximately 50 cm^3, 0.6 cm^3 and 0.06 cm^3) taken from five bars [19]. The RRR values of seven 50 cm^3 specimens taken from the five bars were investigated first; the 0.6 cm^3 specimens were then prepared by sawing and then machining the 50 cm^3 specimens. The 0.06 cm^3 specimens were prepared by swaging the 0.6 cm^3 specimens to 0.15 cm diameter rods. The RRR values of the 50 cm^3 specimens "as received" averaged 10,300 with a range of ± 7 percent about the average. When annealed by heating in air at 400°C for 30 min., the RRR values increased to an average of 11,400 with a range of ± 9 percent. These values are more than twice the value of 5000 obtained on the aluminum samples before recasting. (The specimens used for the RRR measurements before recasting were either 3 or 4 mm diameter, while the 50 cm^3 specimens were 3.6 cm diameter. The average density of the recast aluminum was found to be 2.683 ± 0.005 g/cm^3 as compared to 2.699 g/cm^3 for aluminum that is free of defects. No information is available on the density of the aluminum samples before recasting.) The average RRR value of the nine specimens of 0.6 cm^3 volume (4.1 mm diameter rods) was found to be 9230 with a range of ± 12 percent. The average RRR value of the six specimens of 0.006 cm^3 volume (1.5 mm diameter rods) was found to be 6760 with a range of ± 15 percent. The size effect corrections for these specimens of different sizes would increase the RRR values by 1, 7, and 15 percent, respectively. But, even with these corrections, the two smaller specimens give RRR values that are smaller than the largest specimen. The reduction in the RRR values is attributed to possible contamination during the process of reducing the specimen size. These data show that the recasting process increased the RRR values of the original aluminum samples. However, the RRR values of the recast samples are still not as high as the ultra-purity aluminum samples, SRM-RM-1R and SRM-RM-1C (see Appendix G), which have RRR values of about 16,000.

4.2 Graphite Cells for Containing Aluminum

Figures 16 and 17 show the dimensions of the graphite crucible, lid, and thermometer well that were employed to contain about 358 g of aluminum sample. Because of the relatively high chemical reactivity of molten aluminum the filled graphite cell was completely enclosed in a fused-quartz envelope. Figures 18, 19, and 20 show three types of assembled aluminum-point cells. The relatively large graphite thermometer well accommodates the fused-quartz thermometer well into which the SPRT is inserted during measurement.

4.3 Filling Graphite Cells with Aluminum

The aluminum samples of lot EM 1558, which were 3.2 cm diameter and 16.7 cm long, were inserted directly into the crucible and the lid attached snugly at the top of the crucible. The samples of lot EM 2571,

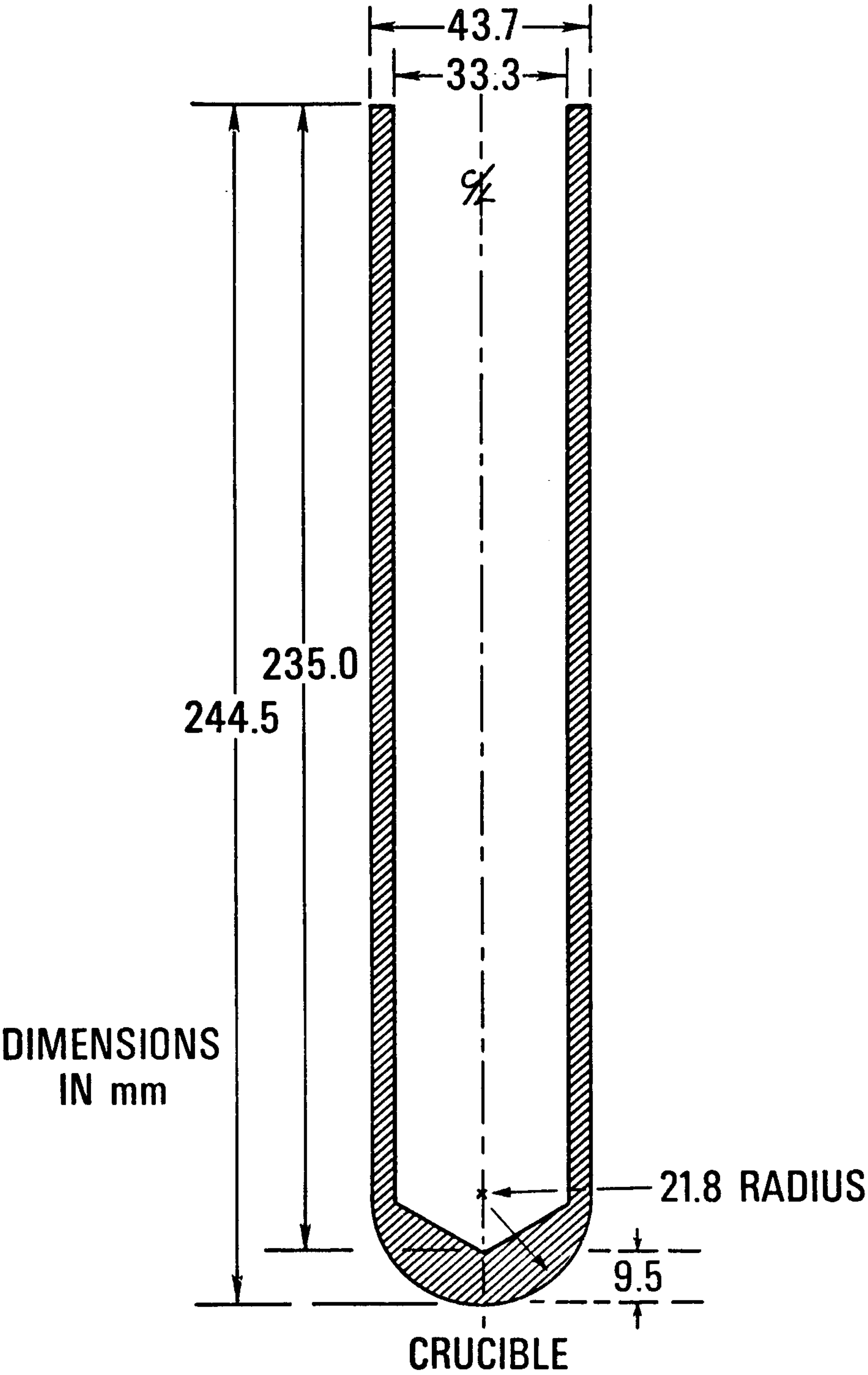

Figure 16. Graphite crucible used to contain aluminum samples in freezing-point measurements.

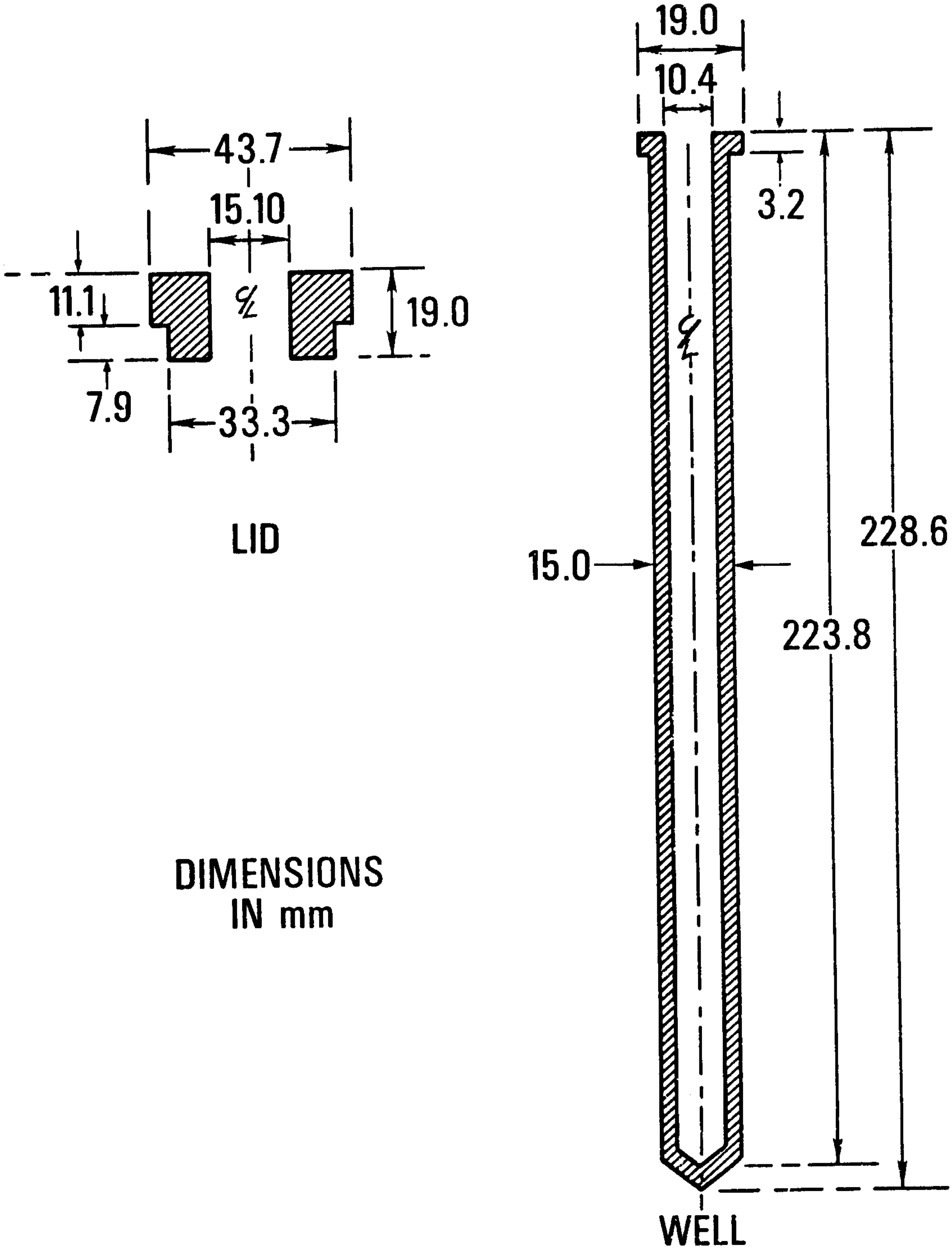

Figure 17. Graphite lid and thermometer well (slide-through type) for the crucible of Fig. 16. [The thermometer well diameter is larger than those of Fig. 2 and Fig. 3 so that a glass tube (fused quartz) could be accommodated inside.]

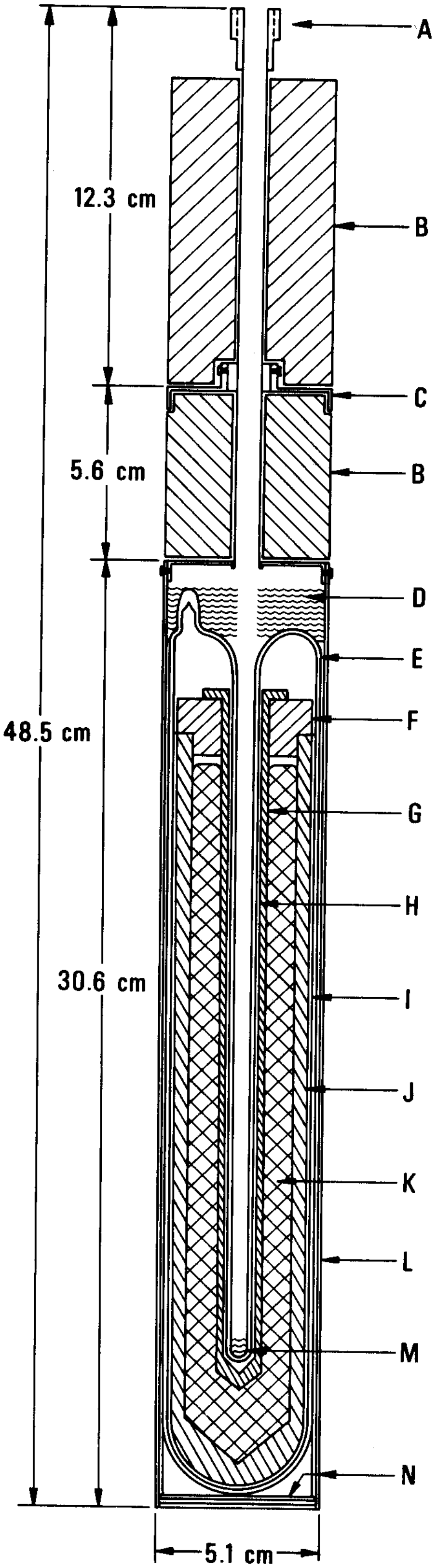

Figure 18. Aluminum-point cell sealed in fused-quartz envelope (Type A cell).

Figure 18. Aluminum-point cell sealed in fused-quartz envelope (Type A cell).

A. Thermometer guide tube (Inconel, 7.94 mm o.d. x 0.13 mm wall) with an adapter at the top for attaching a handle for lifting or lowering the cell into the furnace well.
B. Magnesia (MgO) block insulation.
C. Heat shunts (Inconel flange).
D. Fiberfrax insulation.
E. Fused-quartz outer envelope (48 mm o.d. x 1.5 mm wall).
F. Graphite lid.
G. Graphite thermometer well.
H. Fused-quartz thermometer well (precision bore (7.94 mmi.d.) and continuous with the outer envelope).
I. Fused-quartz fiber, woven tape for cushioning.
J. Graphite crucible.
K. Aluminum sample.
L. Inconel case.
M. Fused-quartz fiber pad for cushioning the thermometer.
N. Fiberfrax paper liner.

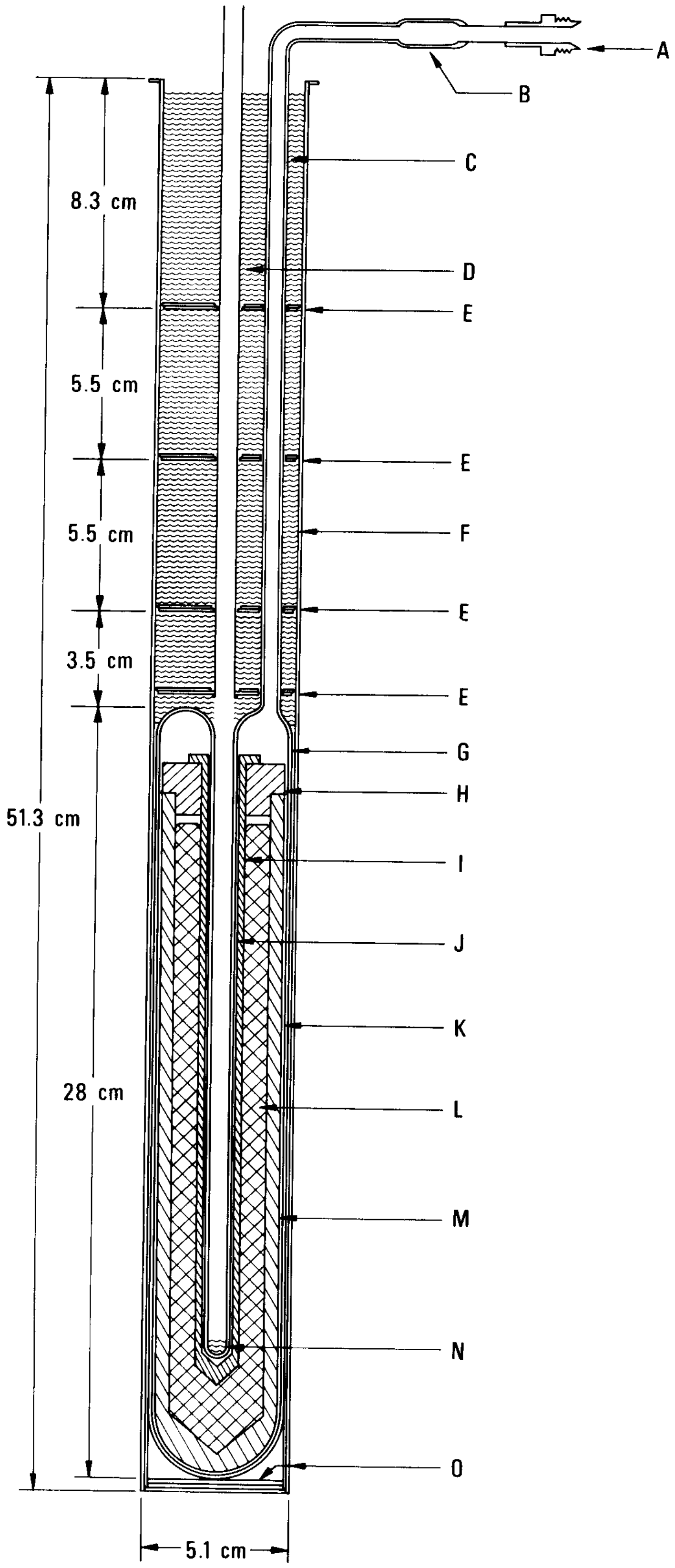

Figure 19. Aluminum-point cell in fused-quartz envelope with Inconel casing (Type B cell).

Figure 19. Aluminum-point cell in fused-quartz envelope with Inconel casing (Type B cell).

A. Connection to high vacuum, purified argon gas source, and manometer.
B. Fused quartz-to-Kovar graded seal.
C. Fused-quartz connecting tube (7.4 mm o.d. x 1 mm wall), outer surface matte finished to minimize radiation piping.
D. Thermometer guide tube (Inconel, 7.94 mm o.d. x 0.13 mm wall).
E. Heat shunts (Inconel disks).
F. Insulation, cut from Fiberfrax blanket.
G. Fused-quartz outer envelope (48 o.d. x 1.5 mm wall).
H. Graphite lid.
I. Graphite thermometer well.
J. Fused-quartz thermometer well (precision bore (7.94 mm i.d.) and continuous with the outer envelope).
K. Fused-quartz fiber, woven tape for cushioning.
L. Aluminum sample.
M. Graphite crucible.
N. Fused-quartz fiber pad for cushioning the thermometer.
O. Fiberfrax paper liner.

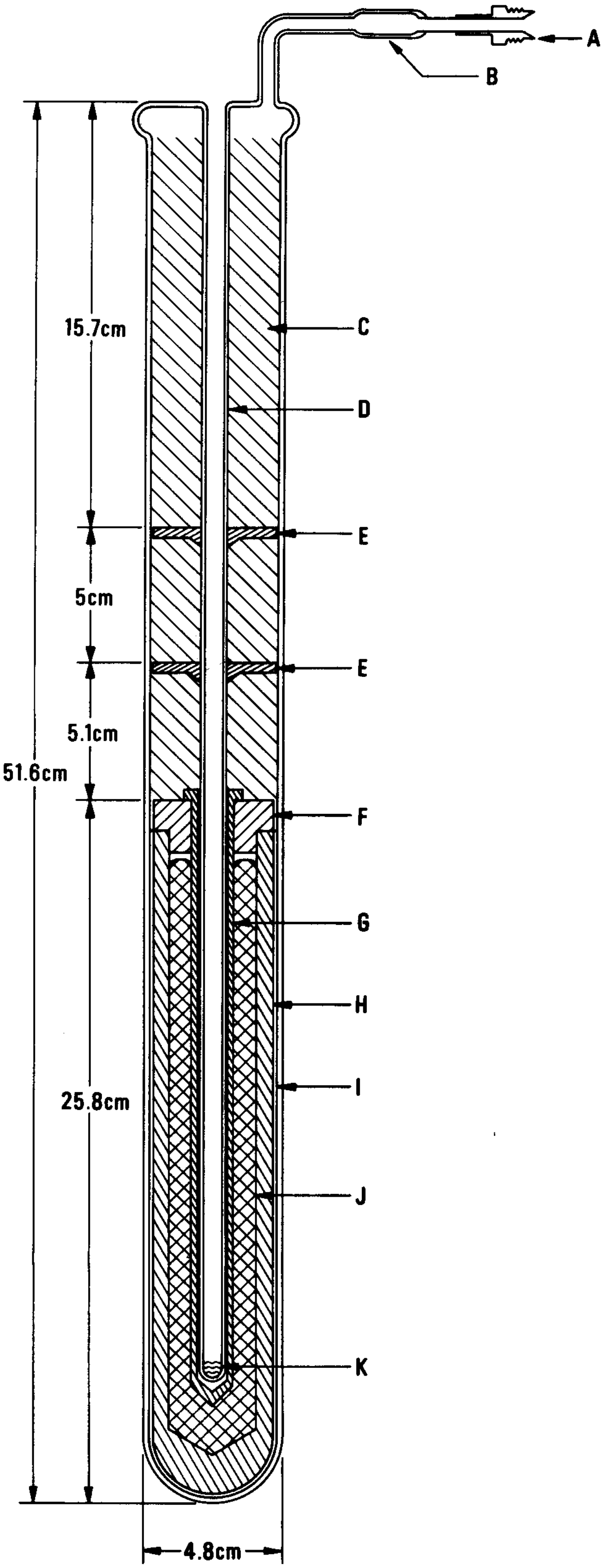

Figure 20. Aluminum-point cell with fused-quartz casing (Type C cell).

Figure 20. Aluminum-point cell with fused-quartz casing (Type C cell).

A. Connection to high vacuum, purified argon gas source, and manometer.
B. Fused quartz-to-Kovar graded seal.
C. Insulation, fused-quartz wool.
D. Fused-quartz thermometer well (precision bore 7.94 mm i.d. and continuous with the outer fused-quartz envelope), outer surface matte finished to minimize radiation piping.
E. Heat shunts, graphite disks.
F. Graphite lid.
G. Graphite thermometer well.
H. Graphite crucible.
I. Fused-quartz fiber, woven tape for cushioning.
J. Aluminum sample.
K. Fused-quartz fiber pad for cushioning the thermometer.

which were 3.8 cm diameter and 11.4 cm long, could not be slipped into the crucible and, hence, were melted into the crucible. The same arrangement that was used for melting zinc into the crucible was employed (see Figure 5), except that the melting occurred at a higher temperature and, similar to the procedure with tin, that the system was continuously pumped to a high vacuum (0.01 torr or less).

The arrangement shown in Figure 8 for zinc was employed to insert the graphite thermometer well into the aluminum sample in the crucible. With aluminum, the system was continuously pumped at high vacuum while gradually increasing stepwise the induction heating power. The pumping system was trapped with liquid nitrogen. When the temperature reached approximately 600°C (a slight red glow in the graphite crucible), the heating power was maintained constant for about one hour at a pressure of about 0.01 torr. The heating power was then gradually increased until the aluminum sample began to melt and the weighted thermometer well began to sink into the crucible. After the sample began to melt, the thermometer well sank into place within about thirty minutes. The heating power was turned off and the sample was allowed to cool. Purified argon was admitted into the system and the filled graphite cell assembly was removed ready for assembly into an aluminum freezing-point cell.

4.4 Aluminum Freezing-Point Cells

Since molten aluminum is highly reactive, the filled graphite cell was completely enclosed in a fused-quartz envelope to protect the aluminum sample. Three types of fused-quartz envelopes were employed (see Figures 18, 19, and 20). The procedures used to assemble the cells in the fused-quartz envelopes were as follows. (Henceforth, for convenience these cells will be referred to as types A, B, and C, respectively.) The fused-quartz envelope was made first to fit the graphite cell. The central thermometer well was made of precision bore fused quartz (8 mm I.D. X 10 mm O.D.). The outer tube was sawed apart at the top. The thermometer well was then sand-blasted on the outer surface starting from about 3 cm from the tip to nearly the top of the well to obtain a matte finish to reduce light (heat) piping [27] from the aluminum-point cell. (Any energy loss through light piping causes the SPRT readings to be low.) The graphite crucible was then inserted into the outer fused-quartz tube using woven fused-quartz fiber tape as a cushion between the crucible and the outer tube. Before the outer tube was resealed at the top, either the fused-quartz thermometer well or the outer tube was shortened so that when assembled the bottom of the fused quartz thermometer well would be about 3 mm above the bottom of the graphite thermometer well. (When the aluminum is melted the buoyant force of liquid aluminum will cause the bottom of the graphite thermometer well to rest against the bottom of the fused-quartz thermometer well. Hence, during operation of the cell the thermal resistance of the original 3 mm gap will no longer exist.) The above allowance for the graphite thermometer well to rise 3 mm was made to compensate for any unknown differences in the thermal expansions of the graphite and fused quartz that were used to fabricate the aluminum-point cell assembly. Also, when the aluminum sample solidifies and contracts on cooling, the 3 mm allowance will permit the sample to rest on the bottom of the crucible and not "hang" on the thermometer well which could cause breakage of the well when the cell is tilted.

Recently, while assembling new type A cells, the bottom of the fused-quartz envelope ruptured on two occasions. Although yet untried, the breakage may possibly be avoided by increasing the gap between the bottom of the graphite thermometer well and the fused-quartz well to 4 mm and by restricting the rise of the graphite well to 2 mm. It is felt that, under certain cooling or heating conditions and certain surface conditions of the graphite in contact with the sample, the graphite crucible and its solid aluminum contents had become confined between the fused-quartz well and envelope. Hence, to avoid strains that would rupture the envelope, a gap should be maintained between the bottom of the graphite well and the fused-quartz well.

Before sealing, the completely sealed type A cell, shown in Figure 18, had the same configuration as that of type B cell of Figure 19. After pumping at high vacuum (10^{-5} torr; see Figure 21 for general arrangement of pumping and gas handling system) for three days with the cell at 670 to 675°C, the cell was filled with purified argon gas and maintained at slightly above atmospheric pressure until the cell cooled to the ambient temperature. The cell was then immersed in water at a known temperature. After the cell reached an equilibrium temperature, the argon pressure in the cell was adjusted so that its pressure would be 1 atm when heated to the aluminum point; the cell was then sealed at the location shown in Figure 18. These type A cells were employed during the preliminary freezing-point experiments. Although the effect of the pressure on the freezing point is relatively small, the temperature uncertainty due to the inability to determine the actual pressure inside the sealed cell was disturbing; therefore, these cells were soon converted to type B configuration shown in Figure 19. Except for the sealed top of the cell, type C aluminum-point cell is very similar to the zinc- and tin-point cells (see Figure 9.)

4.5 Freezing-Point Furnace for Aluminum

The design of the furnace that has been employed with the aluminum-point cells is shown schematically in Figure 22. The furnace is similar in design to those used with the zinc- and tin-point cells (see Figure 10). (The furnace can be used at temperatures below the aluminum point and possibly up to 800°C.) However, there are a number of basic differences in the design. The furnace consists of a central Inconel alloy well (C) for the freezing-point cell. An Inconel disk (5) was "heliarc" welded to seal the bottom end of the Inconel well. An Inconel flange (B) was heliarc welded to the top end of the Inconel well. This Inconel well assembly and the furnace shell (Q) form a vacuum tight enclosure which protects the stack of four cylindrical coaxial blocks of copper [top (H), end (J), center (O), and bottom (U)] from oxidation. The space surrounding the copper blocks was packed with Fiberfrax insulation. The space was evacuated and purged with argon gas several times and finally filled to 1-atm pressure with argon gas.

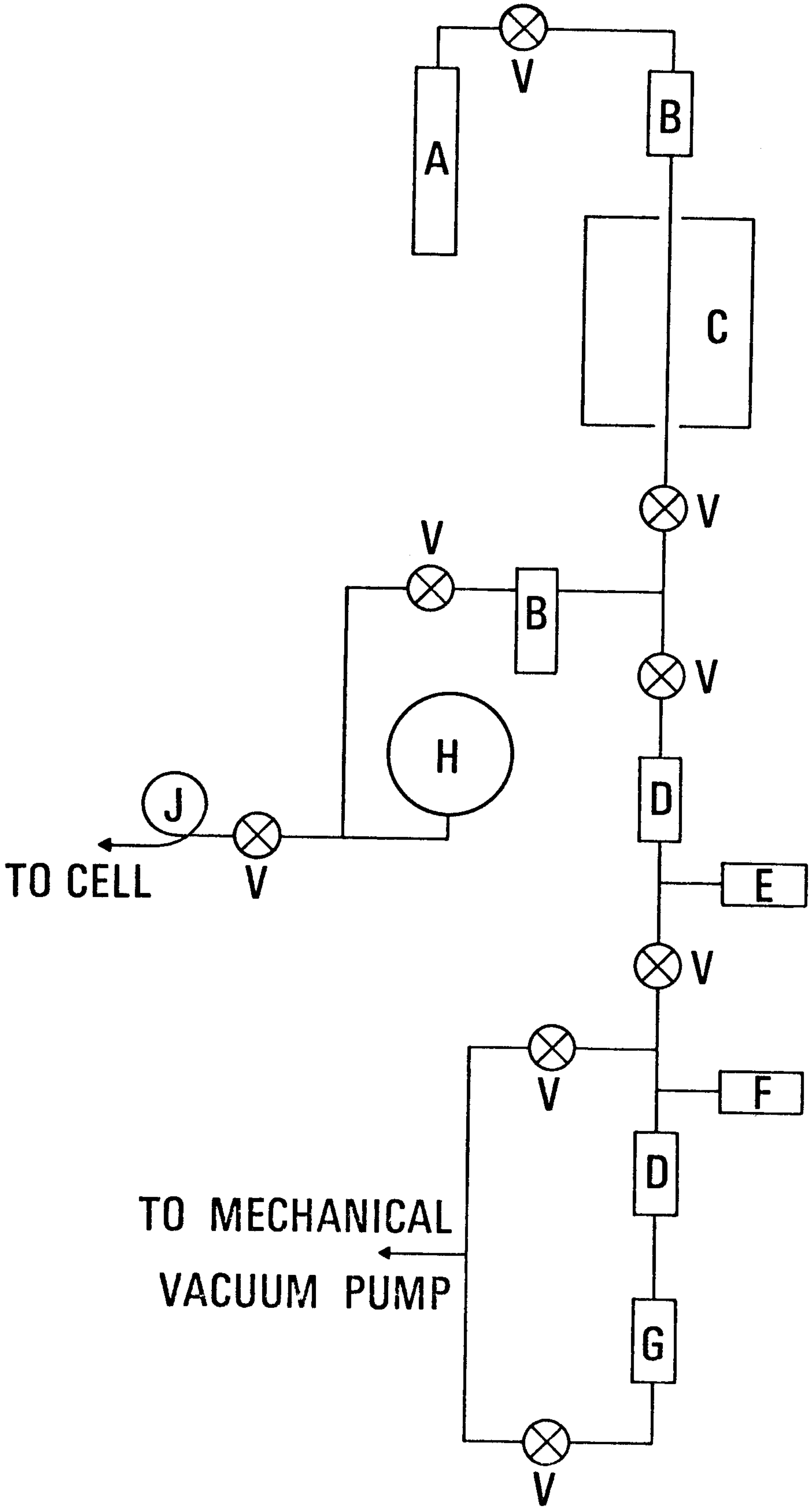

Figure 21. Schematic arrangement of the high vacuum, argon-gas purification and handling, and pressure-measurement system for aluminum-point measurements.

Figure 21. Schematic arrangement of the high vacuum, argon-gas purification and handling, and pressure-measurement system for aluminum-point measurements.

[High-purity argon gas (99.999 percent pure) is first trapped at the oxygen boiling point to remove condensables and reacted first with copper metal then with copper oxide at a furnace temperature of 700°C. The argon gas is again trapped at the oxygen point before use. The purification process is expected to remove any hydrocarbon, oxygen, hydrogen, carbon dioxide, or water.]

A. High-purity argon gas supply cylinder.
B. Cryogenic traps, liquid oxygen.
C. Inconnel tube (packed with copper metal and with copper oxide) in furnace.
D. Cryogenic traps, liquid nitrogen.
E. Vacuum gauge, cold cathode type.
F. Vacuum gauge, thermocouple type.
G. Oil diffusion pump.
H. Dial type manometer, lowest subdivision of scale: 1 mm Hg (torr).
J. Flexible loop of tubing (Inconel, 3.18 mm o.d. x 0.20 mm wall) for connecting to the aluminum-point cell (type B or C).
V. Valve, bellows type.

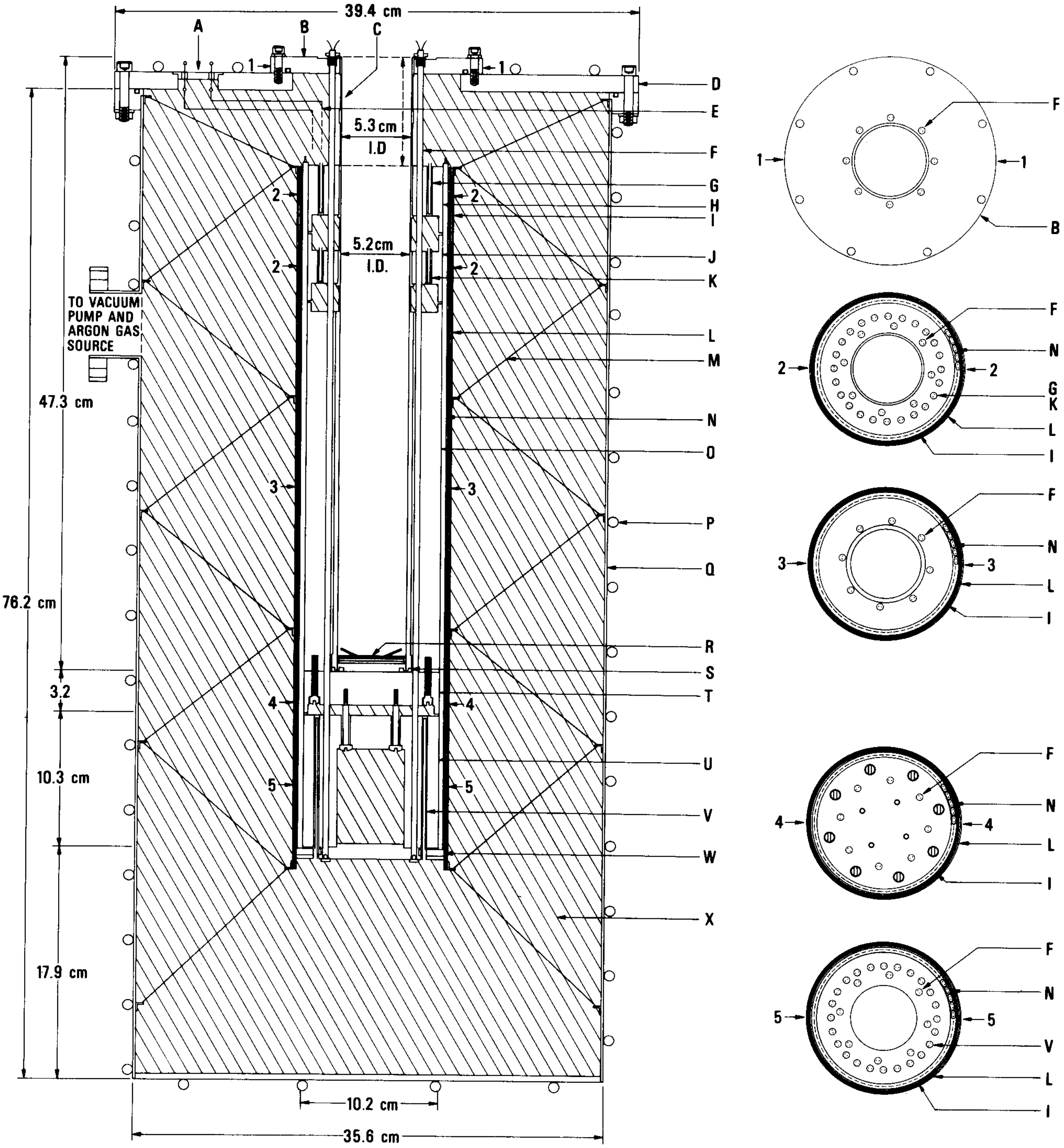

Figure 22. Schematic of furnace used with aluminum-point cells.

Figure 22. Schematic of furnace used with aluminum-point cells.

A. Hermetic insulated posts for electric leads.
B. Inconel flange welded to tube C.
C. Inconel tube furnace core.
D. Brass cover plate.
E. Electric leads (8) to control heaters.
F. Inconel tubes (8, 3.97 mm o.d. x 0.20 mm wall) with thermocouples for temperature control or for monitoring the furnace temperature
G. Heater for the top core block.
H. Top core block.
I. Copper cylinder for holding the main heater M tightly against the copper blocks H, J, O, and U.
J. End core block.
K. Heater for the end core block.
L. Axially centered copper cylinder for receiving the furnace core.
M. Nickel-chromium alloy wire for suspending and centering copper cylinder L.
N. Main heater.
O. Center core block.
P. Coil for circulating cooling water.
Q. Stainless-steel furnace shell.
R. Inconel "spider" for centering the quartz glass cell (type C cell) shown in Fig. 20.
S. Inconel disk welded to tube C.
T. End plate for the center core block.
U. Bottom core block.
V. Heater for the bottom core block.
W. Fused-quartz ring for supporting the main heater N.
X. Fiberfrax insulation.

The main heater (N) extends the whole length of the four copper blocks. The heater was constructed from "U" shaped loops of heater wire and oval-shaped twin-bore alumina tubes. These elements were assembled tightly around the four copper blocks and the "U" shaped loops were heliarc welded in series to form a cylindrical heater. The control heaters for the top, end, and bottom copper blocks were constructed in a manner similar to the main heater from "U" shaped loops of heater wire and round twin-bore alumina tubes. These elements were inserted into circularly arranged holes (see G, K, and V of Figure 22) and heliarc welded in series to form the control heaters. (For more details of the construction, see reference [13]).

The operation of the furnace is very similar to that used for the zinc-and tin-point furnaces. A type K thermocouple (F), with its junction located at the middle of the center block, is used in conjunction with the main heater (N) to control the temperature of the center block at a desired temperature. The temperatures of the top, end, and bottom blocks are controlled relative to that of the center block so that the furnace well temperature is uniform. Automatic temperature controls are used.

4.6 Preparation of Aluminum-Point Freeze

Liquid aluminum has been found to supercool 0.4 to 1.5°C, usually about 0.4 to 0.6°C. Hence, the freeze can be initiated in the furnace without the outside nucleation method used for tin (see Section 3.5). The method for preparing the aluminum-point freeze was the same for the three types of cells that were assembled (see Section 4.4). The completely sealed type A cell, in which the argon gas was sealed to be 1 atm at the aluminum point, did not require control of the argon gas pressure, but cell types B and C required means for controlling and measuring the argon gas pressure at 1 atm with appropriate accuracy. The effect of pressure on the freezing point of aluminum is 7.1 mK/atm or 9.3 μK/torr [13]. During operation the pressure is controlled to within ± 0.1 torr.

Except for operating at a higher temperature, the aluminum freeze is prepared by a procedure very similar to that used with zinc.

1.) With type B and C cells, if the argon gas pressure had been below ambient during storage, the cell is evacuated to remove air, water vapor, or other gases that may have leaked into the cell. (Figure 21 shows schematically the system that is used for pumping, for filling with argon gas, and for measuring the gas pressure.)

2.) The furnace control is set 5°C above the aluminum point to melt the sample overnight. During this time, the evacuation of the cell is continued.

3.) Next morning a monitoring SPRT is inserted into the cell and purified argon gas is introduced to pressurize the freezing process at 1 atm. [The monitoring SPRT and other SPRT's for measurement at the aluminum point were specially constructed [12, 40]. The insulation supports for the platinum thermometer resistor and leads were either fused quartz or sapphire and the thermometer sheath is fused quartz.] For the aluminum-point cell, high-purity grade argon (99.995 percent) is first cooled to the boiling point of oxygen to remove moisture and other condensable impurities (see Figure 21). The gas is then passed through a tube containing, successively, copper metal and cupric oxide held at 700°C. The copper metal should remove any oxygen and the cupric oxide should react with any hydrogen, hydrocarbon, or other organic impurities. To remove any carbon dioxide or water that was formed the gas is again cooled to the boiling oxygen temperature before being introduced into the aluminum-point cell.

4.) To start the freeze, the furnace temperature control is reset to about 2°C below the freezing point.

5.) After the monitoring SPRT indicates that recalescence has occurred, the SPRT is removed and two fused-quartz rods are inserted successively into the thermometer well for about 5 min each to induce an inner freeze immediately next to the thermometer well.

6.) During this time, the furnace temperature control is reset to 1°C below the aluminum freezing point.

7.) After withdrawing the second fused-quartz rod, the monitoring SPRT is inserted stepwise into the thermometer well. Since the SPRT will cool considerably between the time it is withdrawn from any auxiliary preheat furnace and inserted into the aluminum-point cell, the SPRT is preheated instead in the section of the thermometer guide tube which is maintained close to the furnace temperature. The SPRT is inserted initially to a location where its tip is about 3 cm above the graphite crucible lid. After about 10 min the monitoring SPRT is inserted 5 cm and after another 5 min another 5 cm and so on until the tip of the SPRT is at the bottom of the thermometer well. About 15 to 20 min are required after completion of the insertion to be certain that the monitoring SPRT has attained temperature equilibrium.

8.) After completion of the reading, the monitoring SPRT is withdrawn first from the cell to a location where the thermometer tip is about 3 cm above the graphite crucible lid. After about 5 min the SPRT is withdrawn 5 cm and after another 5 min another 5 cm and so on until the SPRT is completely out of the cell. The SPRT is then inserted into an auxiliary annealing furnace held at 480 °C. [In platinum resistance thermometry it is standard practice to determine the SPRT resistance at the unknown temperature and then at the triple point of water in order to determine the resistance ratio, $W(t) = R(t)/R(0°C)$. The aluminum point is high enough in temperature so that, if the SPRT is withdrawn quickly out of the cell, lattice defects will be quenched into the platinum resistor. By removing the SPRT in steps, as described above, the quenched in defects are expected to be less. Before resistance measurements at the triple point of water is made, the SPRT is annealed at 450 to 480°C for about 30 min. The withdrawing of the SPRT from a furnace at 480°C and cooling at ambient temperature show very little effects (i.e., <2 parts in 10^7) of quenched-in lattice defects [1].]

9.) After removing the monitoring SPRT from the aluminum-point cell, the test SPRT's are each inserted, the resistance readings obtained, and then removed from the cell and annealed SPRT. Measurements of as many as seven test SPRT's have been made with a single aluminum freeze.

10.) After the measurements on the last test SPRT are completed, measurements are then made on the monitoring SPRT. [At present, SPRT's are not regularly calibrated at the aluminum point; however, in test calibrations, this second reading with the monitoring SPRT has not differed from the first reading by more than 0.2 or 0.3 mK.]

When the aluminum-point freeze is prepared as outlined above, freezes of about 10 to 12 hours' duration are obtained. Freezes of longer duration have been obtained by controlling the furnace temperature closer to the freezing-point temperature. Figure 23 shows freezing curves that were obtained with five different cells containing the aluminum samples described in Sections 4.1 and 4.4. Although results of consecutive insertion and reading of an SPRT have not been obtained as of this writing, the results of Figure 23 indicate that consecutive readings obtained over several hours should not differ by more than about 0.1 mK.

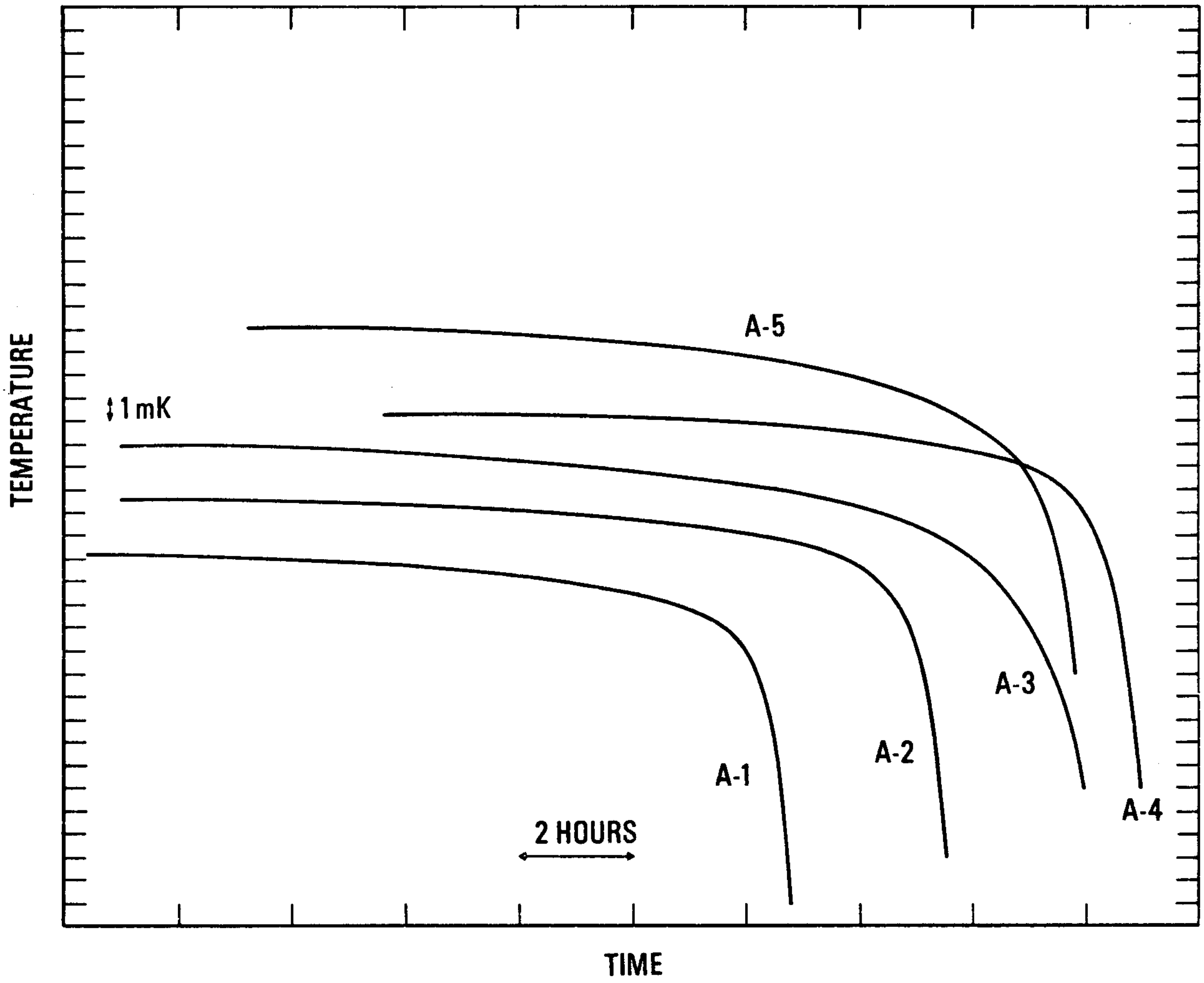

Figure 23. Typical freezing curves of five aluminum samples recorded starting approximately fifteen minutes after the insertion of an SPRT in the cell.
[Measurements were obtained with an a-c bridge. The curves are displaced both vertically and horizontally; they are intended to show only the relative temperatures within the individual freezing curves].

5. Cadmium Freezing Point

The freezing point of cadmium, a secondary reference point, is assigned the value 321.108°C (594.258K) on the IPTS-68 [36]. The metal behaves in many respects similar to zinc. Like zinc, the vapor pressure of cadmium at its melting point is relatively high (15 Pa [28]). Since the metal and its compounds are toxic, cadmium should be handled with caution.

5.1 Cadmium Sample

The SRM-746 cadmium is normally issued as a vapor-pressure standard in the form of rods 6.4 mm diameter and 64-mm length. Enough rods were obtained from the NBS-OSRM to assemble two freezing-point cells for test measurements. On the basis of chemical analyses and RRR measurements, the material is considered to have a purity greater than 99.999 percent (see SRM-746 certificate, Appendix H.)[7]

A selected lot of cadmium was used as the starting material in the preparation of the SRM-746 samples. The starting material was vacuum distilled twice followed by at least twenty zone refining passes. The zone refined units were homogenized into one lot (approximately 45.4 kg) and cast into 14 billets of 4.8-cm diameter and 30.5 cm length. The billets were then extruded into 6.4-mm diameter rods using a tungsten carbide die. The rods were cut into 45.7-cm lengths, etched, washed, and dried. The pieces were packaged in individual plastic tubes and identified with respect to the billet and the position in the succession of pieces that were extruded from the billet (e.g., piece E-4 is the fourth piece extruded from billet E). Except for two billets, 29 or 30 pieces were obtained from each billet. The supplier furnished emission spectrochemical analysis on samples taken from the starting 45.4 kg lot of zone refined cadmium before casting into billets and samples taken from each of the 14 billets. The analysis is summarized in Table XIV.

Table XV shows the results of mass spectrometric analysis of specimens from pieces A-1 and G-12. These results are generally consistent with the emission spectrometric analysis given in Table XIV. The relatively high Cr impurity found by the mass spectrometric method was not reported in the emission spectrometric analysis.

V.A. Deason and R.L. Powell (at the time with the Cryogenic Properties of Solids Section of the NBS at Boulder, Colorado) investigated the RRR of the 6.4-mm diameter specimens from all of the billets and found the values to range from 3,370 to 24,000. They estimated the purity from the results to be from 99.9991 to 99.9998_7 percent [7, 9, 10].

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[7] The NBS-OSRM obtained from the supplier 45.4 kg of high-purity cadmium in the form of rods 6.4-mm diameter by 45.7-cm length (384 pieces), under NBS Order No. S-457534-67. The material is identified by the supplier as Lot No. HPM 7541, Contract No. EMS 1426.

Table XIV

Emission Spectrochemical Analysis of the Cadmium Samples (From the Assay Certificate of Supplier, Lot HPM 7541, November 25, 1967

	Impurity Elements, in ppm							
	Cu	Mg	Fe	Si	Ag	Pb	Al	Ca
Starting Material	<0.1	0.1	ND[a]	0.1	0.1	ND[a]	ND[a]	ND[a]
Billet								
A	0.1	0.1	ND	0.2	0.1	ND	ND	ND
B	0.1	0.2	0.2	0.5	<0.1	ND	ND	ND
C	0.1	0.2	0.1	0.5	<0.1	ND	ND	ND
D	0.1	0.1	0.2	0.5	0.1	ND	ND	ND
E	0.2	0.1	0.2	0.3	0.1	ND	ND	ND
F	0.1	0.2	0.1	0.3	0.1	ND	ND	ND
G	ND	0.1	ND	0.3	0.3	ND	0.2	0.1
H	ND	0.1	ND	0.2	0.1	ND	0.2	ND
I	ND	<0.1	0.2	0.3	<0.1	0.3	ND	ND
J	ND	<0.1	0.1	0.3	<0.1	0.3	0.2	ND
K	ND	<0.1	ND	0.3	0.1	0.5	ND	ND
M	<0.1	<0.1	ND	0.2	<0.1	0.5	ND	0.1
N	0.1	<0.1	0.1	0.3	<0.1	ND	ND	0.1
O	0.1	0.1	0.3	0.3	0.1	ND	ND	0.1

[a] ND = not detected. No information is available on the limits of detection of the elements.

Table XV

Mass Spectrometric Analysis of Cadmium Specimens from SRM-746 (Lot HPM 7541)[a]

	Specimen[b]	
Element	A-1 (in ppm)[c]	G-12 (in ppm)[c]
Li	0.004	0.005
C[d]	0.1	0.1
O[d]	2	1
Na[d]	2	3
Mg	0.1	0.07
Cl	0.2	0.1
K[d]	4	3
Ca[d]	0.6	0.6
V	0.04	0.07
Cr	0.4	0.4
Cu	0.07	0.05
Zn	0.1	0.07
As[e]	0.1	0.1
Rb[e]	0.1	0.1
Pb	0.8	0.4

(contd)

Table XV (continuation)

Cadmium interfered with the following elements;
the values are estimated upper limits:

Element	PPM	Element	PPM
B	0.004	Ni	0.05
N	0.06	In	0.6
F	2	Sb	0.2
Ne	0.01	Te	0.9
Al	5	I	0.4
Si	3	Cs	0.2
P	0.04	Ta	9
S	0.2	Pt	0.3
Ar	0.6	Au	10
Sc	0.4	Th	2
Ti	0.2		

Table XV (continuation)

The following values are the upper limits of elements not detected:

Element	PPM	Element	PPM
Be	0.001	Sm	0.2
Co	0.02	Eu	0.08
Ga	0.02	Gd	0.09
Ge	0.04	Tb	0.02
Se	0.03	Dy	0.08
Br	0.03	Ho	0.02
Kr	0.02	Er	0.07
Sr	0.01	Tm	0.02
Y	0.02	Yb	0.08
Zr	0.02	Lu	0.03
Nb	0.02	Hf	0.07
Mo	0.04	W	0.09
Tc	0.01	Re	0.04
Ru	0.04	Os	0.07
Rh	0.01	Ir	0.05
Pd	0.08	Hg	0.1
Ag	0.1	Tl	0.05
Sn	0.7	Bi	0.03
Xe	0.06	Po	0.04
Ba	0.5	Ra	0.04
La	0.04	Ac	0.04
Ce	0.04	Pa	0.04
Pr	0.04	U	0.04
Nd	0.1	Pu	0.04
Pm	0.04		

There was complete interference with Mn and Fe.

Table XV (continuation)

[a] The analysis was performed by C.W. Mueller and P.J. Paulsen, Analytical Chemistry Division, National Bureau of Standards (March 25, 1970).

[b] The specimens were cut with a saw, filed with a new unused file and then etched in 10 percent solution of nitric acid to remove surface contamination. The samples were pre-sparked before analysis to further lower surface contamination.

[c] Due to lack of a comparison standard, all results are based on sensitivity factors. Therefore, the results can be expected to be in error by a factor of 3 to 10.

[d] These elements were found in all samples run by spark source mass spectrography; the values given should be considered as upper limits since they may represent instrument contamination and other factors.

[e] Results of possible memory from previous analyses; the values given should be considered as upper limits.

5.2 Graphite Cells for Cadmium

The SRM-746 cadmium samples were placed in two graphite cells of different thermometer well dimensions. One cell had the thermometer well-lid dimensions given in Figure 3; the other cell had larger thermometer-well dimensions, 11.3 mm I.D. X 14.5 mm O.D., to accommodate calibrations of special thermometers in holders. The former cell was filled with about 1670 g of Cd and the latter cell with about 1400 g.

5.3 Filling Graphite Cells with Cadmium

The procedure for filling graphite crucibles with cadmium samples was similar to that used with zinc samples (see Section 2.3). The vapor pressure (about 15 Pa [28]) of cadmium at its melting point is high enough to require argon gas to inhibit vaporization. Since the cadmium sample rods were 6.4-mm diameter, some rods were packed directly into the crucible and the remainder were placed in the funnel (see Figure 5). After pumping at about 200°C for an hour, the bell jar was filled with argon gas to about 0.3 atm pressure and the rods in both the crucible and the funnel were quickly melted (in about fifteen minutes). (A cadmium metal mirror formed at the top of the bell jar during this process. In one case a thin brown ring also formed around the bell jar near the top of the crucible.) The filled crucible was allowed to cool nearly to room temperature and the bell jar was filled to atmospheric pressure with argon gas. The installation of the thermometer wells in both filled crucibles involved sliding the well through the central hole in the lid as shown in Figure 8. However, instead of "weighting" the thermometer well into the melted cadmium, the "push rod" technique was used. The filled crucible with attached lid was inserted into the special borosilicate glass holder of Figure 7 and the thermometer well was positioned on the push rod and inserted part way into the hole in the lid. After thoroughly purging the system with purified argon, the cadmium was melted, and the thermometer well was then inserted fully through the lid (see the procedure used with zinc in Section 2.3).

5.4 Cadmium Freezing-Point Cells

The cadmium-point cells were assembled by installing the graphite cells containing the cadmium samples inside borosilicate glass holders (see Figure 4). The assembly procedures and the dimensions of the completed cells were similar to those of zinc cells (see Section 2.4 for details). However, the SPRT guide tube diameters (see Figure 9) were different for the two cells; they were selected to match the inside diameters of the respective graphite thermometer wells which were different (see Section 5.2).

5.5 Freezing-Point Furnace for Cadmium

Since cadmium melts below the melting point of aluminum, the aluminum core furnaces used for realizing the zinc point and the tin point (see Figure 10 and Section 2.4) could be used with the cadmium-point cell. However, since the NBS aluminum core furnaces are used regularly for calibrating SPRT's at the tin point and the zinc point, the testing of the cadmium-point cells was actually done in the furnace used for realizing the aluminum point (see Figure 22 and Section 4.5).

5.6 Preparation of Cadmium-Point Freeze

Liquid cadmium has been found to behave very similar to liquid zinc and to supercool not more than 0.5 K. Hence, the freeze can be initiated by lowering the furnace temperature a few degrees below the freezing point and, when the freezing starts, re-adjusting the furnace temperature to 1°C below the freezing point to prolong the freezing time. The effect of pressure on the freezing point of cadmium is about 50 percent larger than that of zinc (see Table III). The effect is large enough to require the pressure over the freezing metal to be controlled instead of being allowed to follow any change in the ambient pressure. The effect of pressure on the freezing temperature of 6.2 mK/atm corresponds to 8.2 μK/torr. In the Washington, D.C. area the barometric pressure almost never averages 760 torr and during a storm can change 20 torr or more. A change of 20 torr corresponds to 0.16 mK change which can be readily detected on the SPRT. The effect of pressure and the problem of toxicity can be minimized by sealing the cell in borosilicate glass (see Figure 18). A manostat, similar in design to that described by Brombacher, et al. [3], was used to control the helium-gas pressure over the cadmium cell to about ±0.1 torr. The pressure was controlled through the gas inlet tube B of the freezing-point cell (see Figure 9).

The cadmium freeze is usually prepared as follows:

1.) The helium-gas pressure over the cadmium metal in the cell is set to control at 1 atm.

2.) The furnace temperature control is set 5°C above the cadmium point to melt the sample overnight.

3.) Next morning an SPRT is inserted into the cell to monitor the freezing process.

4.) To start the freeze, the furnace temperature control is set to control 5°C below the freezing point.

5.) When the SPRT indicates that recalescence has occurred, the SPRT is removed and two borosilicate glass rods are inserted successively into the thermometer well for about 5 min each to induce an inner freeze immediately next to the thermometer well.

6.) During this time the furnace temperature control is reset to control 1°C below the cadmium freezing point.

7.) After withdrawing the second glass rod, the monitoring SPRT is inserted into the cadmium-point cell. Figure 24 shows the results of monitoring a complete freeze; the temperature changed about 0.4 mK over most of the freezing range. Over the first 75 percent of the freeze the temperature change was about 0.2 mK.

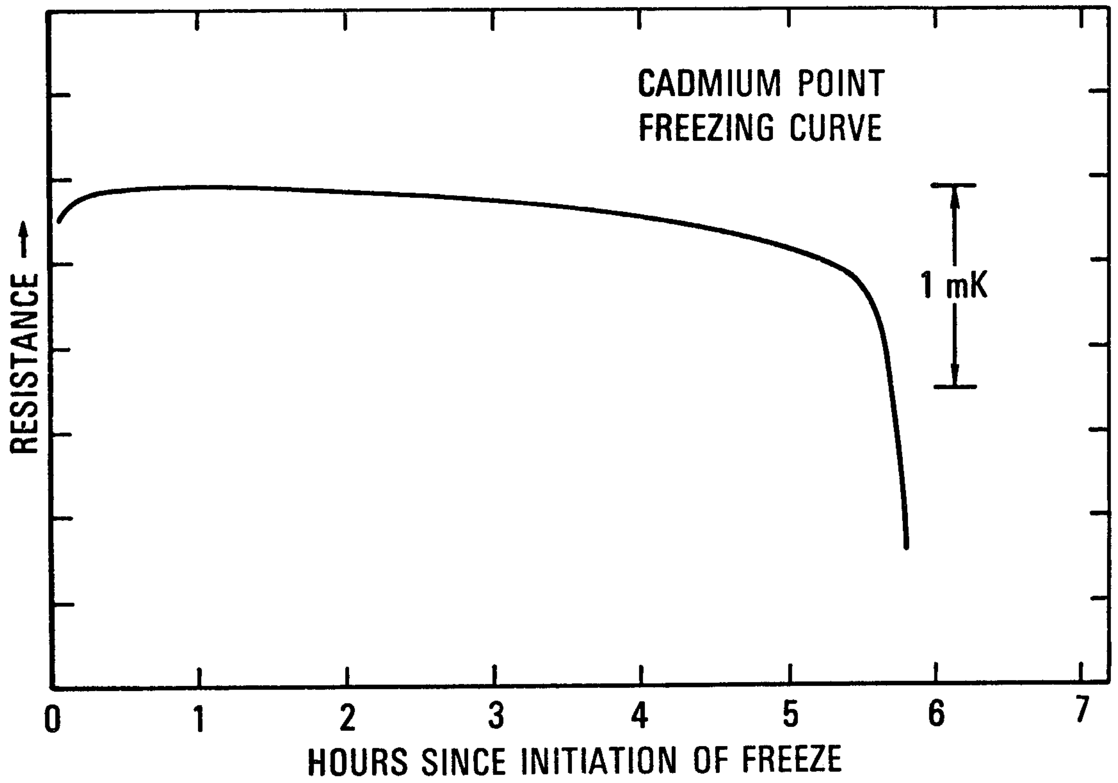

Figure 24. The freezing curve of cadmium (SRM-746)

[The head of the SPRT was adapted for coaxial connectors and an a-c bridge was used. The furnace was controlled to be 1 K below the cadmium point. The mass of cadmium was 1668g].

The cadmium point has not as yet been employed in routine measurements for checking the calibration of SPRT's. However, the results of repeated measurements with an SPRT showed the test measurements to be highly reproducible (see Figure 25). The total change in the observed resistances during seven hours since initiation of the freeze is shown to be about 0.2 mK.

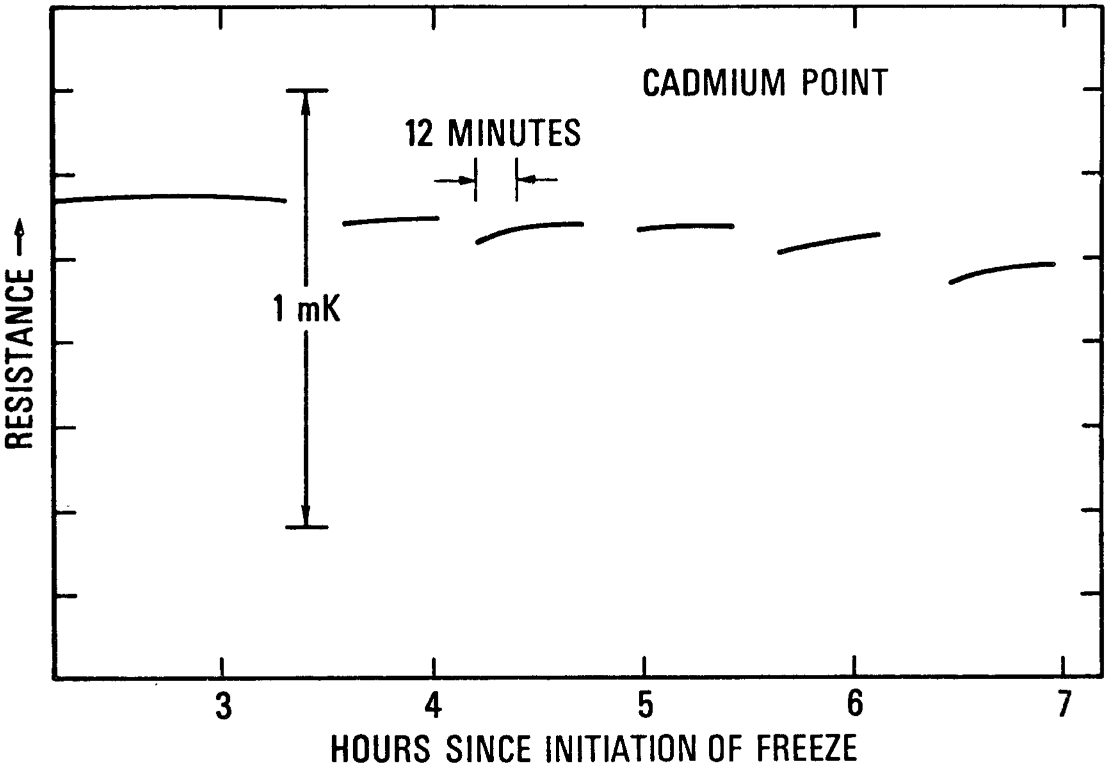

Figure 25. Consecutive measurements of the resistance of an SPRT in a single cadmium freeze (SRM-746).

[An a-c bridge was employed in the measurements. Following each equilibruim resistance measurement, the SPRT was completely withdrawn from the cadmium-point cell and then quickly reinserted into the cell. The data show the somewhat cooled SPRT to come to equilibrium rapidly.]

6. Mercury Triple Point

The state of thermodynamic equilibrium between the solid and liquid mercury at 1 standard atmosphere of pressure is assigned the value -38.836°C (234.314 K) on the IPTS-68 [36]. The freezing-point measurements at 1-atm of pressure with mercury require a closed dry-gas handling system or other procedures to avoid condensation of moisture in the sample; however, the moisture condensation problem could be avoided by using sealed cells of mercury and making "triple-point" measurements. When the mercury cells are sealed, accidental contamination by metal impurities is also avoided. The triple point of mercury will have the value -38.841°C (234.309 K) when the above value for the freezing point at 1-atm pressure is adjusted for the effect of pressure on the freezing point [36] (see also Table III).

This section describes the apparatus and procedures that were used to assemble mercury triple-point cells. Equipment and techniques for realizing the triple point of mercury by freezing and by melting techniques are also described. In the freezing experiment, the principal difference between mercury and the other metals discussed earlier (zinc, tin, aluminum, and cadmium) is that the freezing curve for mercury is observed at its triple-point pressure while with others the freezing curves are observed at 1-atm of pressure. (Henceforth, unless specifically indicated, any reference to freezing points or freezing-point measurements with mercury are at "triple-point conditions" with no external pressure other than the vapor pressure of mercury. Similar triple-point conditions apply when reference is made to melting-point measurements with mercury.)

6.1 Mercury Samples

Mercury samples, designated SRM-743, are available in 0.68 kg units sealed under argon in soft-glass ampoules (see Appendix I). Mercury can readily be made purer than 99.9999 percent by nitric acid washings followed by triple distillation, the first and second distillations being conducted with small amounts of air bubbling through the boiling mercury and the third distillation being conducted at high vacuum. Potassium or sodium hydroxide washings may precede the nitric acid washings to remove such metals as tin, zinc, and lead. It was found, using radioactive zinc, copper, and cobalt, that these elements can be removed by nitric acid washings to levels below 1 in 10^{11}, 10^{10}, and 10^{10}, respectively, in each case the limiting sensitivity of the analytical method that was used [18]. The distillation in presence of air oxidizes the base metals dissolved in the mercury; the low-temperature vacuum distillation minimizes the volatilization of the noble metals and leaves these metals behind.

Mercury purified by procedures as outlined above was received from the supplier in specially reinforced polyethylene bottles with leak-proof screw caps containing about 0.68 kg each. The assay certificate that accompanied the sample is summarized in Table XVI. On the basis of the analysis and assuming that other elements are not present, the total impurity content is less than about 10 parts in 10^9. However, small amounts of foreign material that appeared to be possibly polyethylene powder or other organic solids were found to be floating on the mercury surface in each of the polyethylene bottles. The material was returned to the supplier to be re-packaged in soft-glass ampoules under argon atmosphere. This re-packaged mercury is designated SRM-743.[8]

To obtain information on the reproducibility of the triple point of mercury, samples from two other sources were investigated along with the SRM-743 mercury. The other two mercury samples were purified by procedures very similar to those outlined above for SRM-743. One of the samples is the NBS density standard mercury which had been prepared over twenty years ago. The other mercury sample was prepared recently in the "Pressure Section" of the NBS. Comparison of their triple points showed that the values are well within ± 0.1 mK of the average.

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[8] This high purity mercury was originally received from the supplier in two lots of about 45 kg each in the polyethylene bottles containing about 0.68 kg each 65 bottles under NBS Order No. S-198495-71 and 67 bottles under NBS Order No. S-208195-72). The supplier identified the two lots HP 10,009 and HP 10,010 as being the same under lot No. EM 2279 and furnished one assay certificate. Both lots were returned to the supplier to be re-packaged in flame sealed soft-glass ampoules. After processing, 132 ampoules containing 0.68 kg each were obtained.

Table XVI

Emission Spectrochemical Analysis of the Mercury Sample (SRM 743)

(From the Assay Certificate of Supplier)[a]

Element	Sample Lot EM 2279 (in ppm)
Al	<0.001
Ca	<0.001
Cu	<0.001
Fe	<0.001
Pb	<0.001
Mg	<0.001
Si	<0.005
Ag	<0.001

[a] Date: January 24, 1972

6.2 Borosilicate-Glass Cells for Mercury

Soft glass is recommended over borosilicate glass for storing mercury [18]. However, for mercury triple-point cells, soft glass is less resistant to rapid temperature changes and, therefore, more susceptible to breakage than borosilicate-glass cells. To test whether borosilicate glass causes significant contamination of the high-purity mercury, mercury cells of borosilicate glass were made and the triple points were observed by the progressive freezing method as employed with zinc, tin, aluminum, and cadmium. The tests showed that borosilicate glass over a period of three years has not caused noticeable change in the freezing temperatures to indicate contamination.

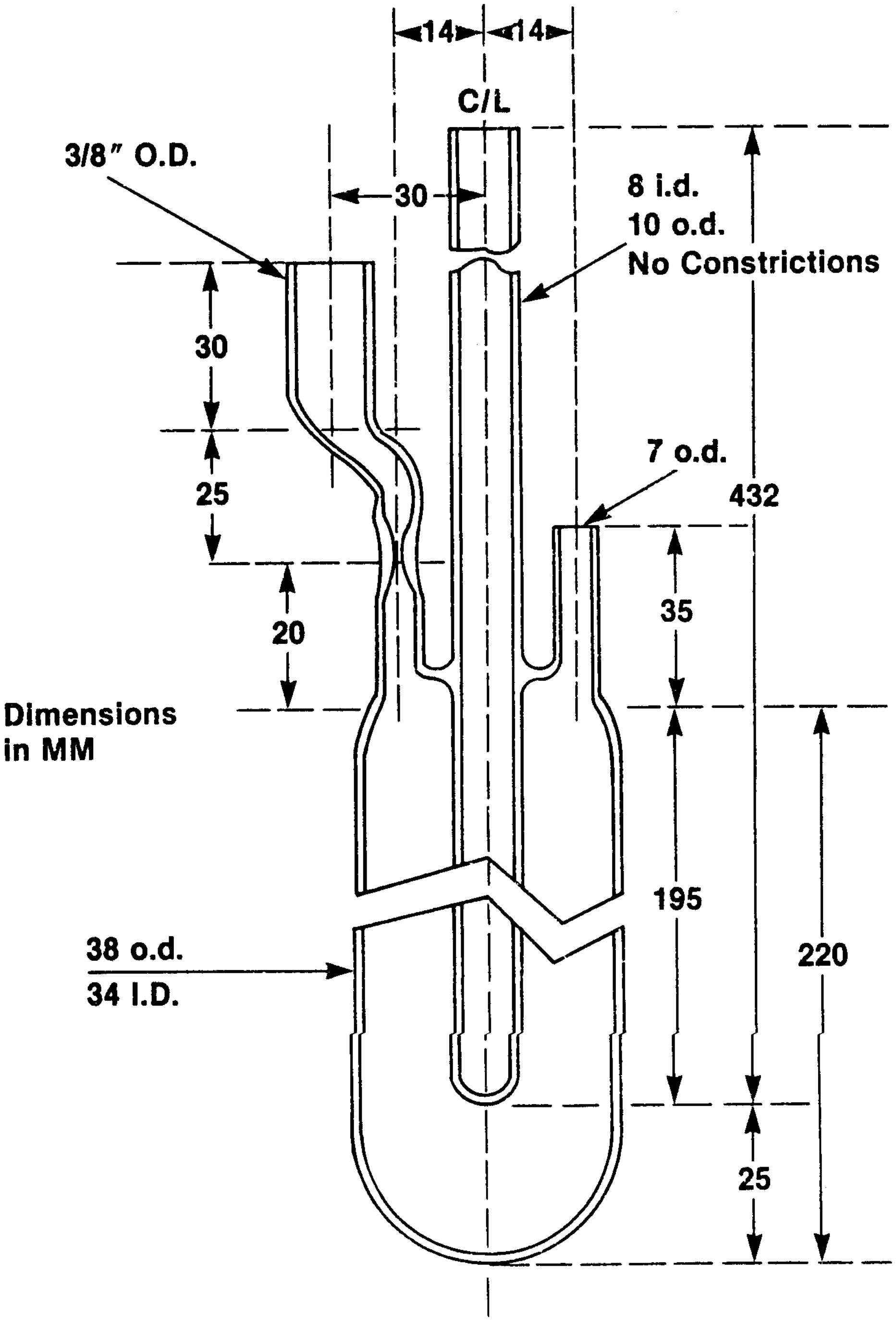
Figure 26 shows schematically the borosilicate-glass cell for mercury triple-point measurements. The two entrance tubes into the cell were required for thorough steam cleaning of the cell before filling with mercury. After cleaning, the shorter entrance tube was sealed and the cell was filled through the larger entrance tube (see Section 6.3). Approximately 2.3 kg of mercury were used per cell. When the SPRT was inserted in the cell, the height from the mid-point of the SPRT coil to the upper mercury surface, i.e., the "SPRT immersion", was 15.5 cm.

To investigate the possible application of stainless steel for mercury triple-point cells, two type 304 stainless-steel cells with dimensions very similar to those of the borosilicate-glass cells were also constructed. Since we have as yet no "long term" information on stainless-steel mercury cells, this paper will deal principally with borosilicate-glass mercury cells. However, some preliminary results with stainless-steel cells will be shown.

6.3 Filling Borosilicate Glass Cells with Mercury

Figure 27 shows schematically the arrangement used to fill the mercury cells by distillation from a reservoir. To avoid changing the chemical composition of the original mercury source, the required amount of sample was weighed into the reservoir and all of the sample was distilled into the cell.

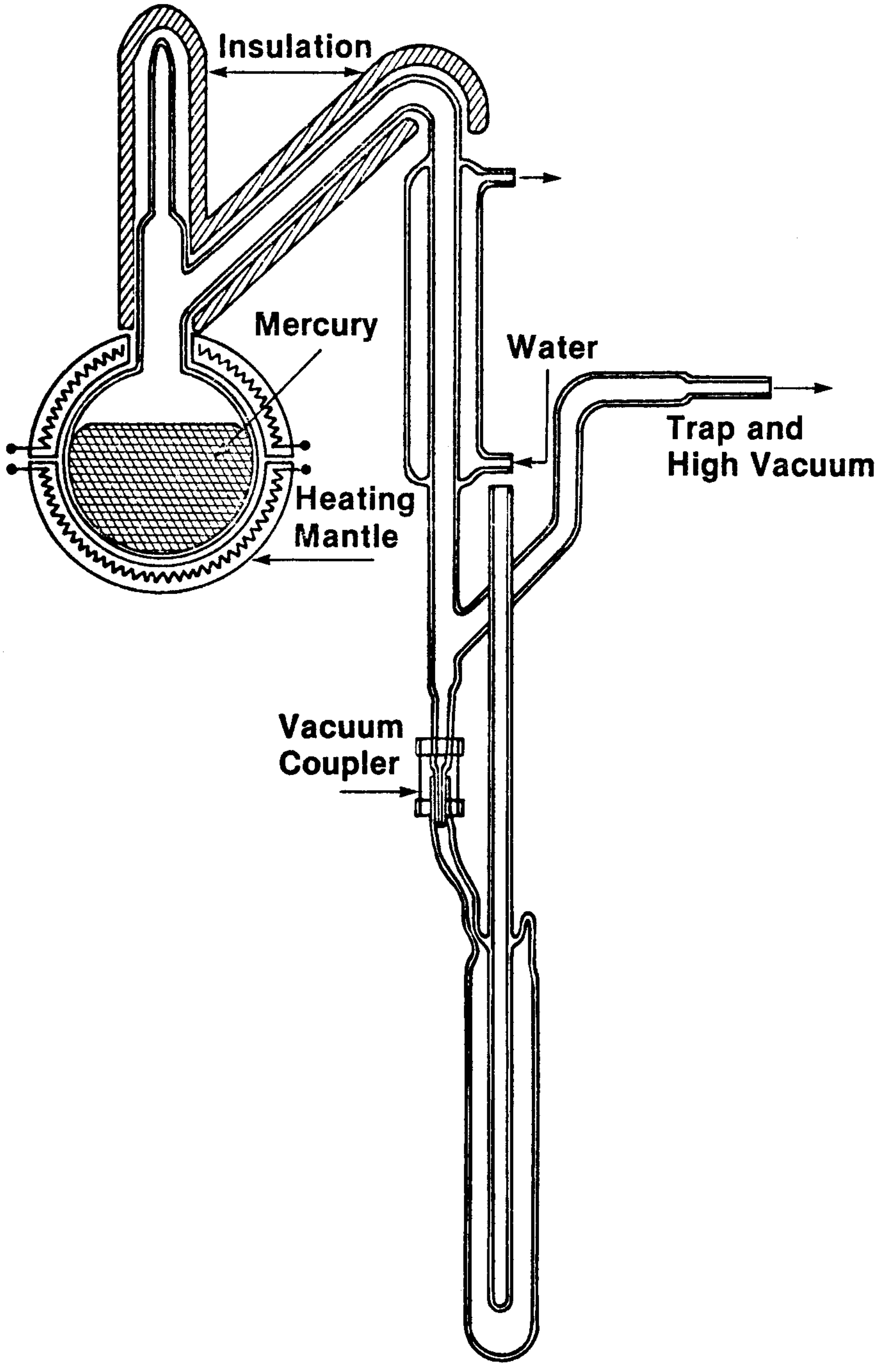
The procedure used for filling mercury cell was as follows. The borosilicate-glass distilling apparatus was first treated with reagent-grade nitric acid to remove any metallic impurities. After thoroughly rinsing with distilled water, the apparatus was then steam-cleaned for about eight hours. The filling tube at the top of the reservoir was sealed with a Teflon coupling and the distilling apparatus was mounted with a steam-cleaned mercury cell as shown in Figure 27. The system was freed of moisture by pumping and warming. After thorough drying, dried nitrogen was admitted and the reservoir was quickly filled with a requisite amount of mercury and the filling tube to the reservoir flame sealed. (The filling tube was made long enough to permit a number of sealing and opening by breaking the tube.) The mercury cell was then heated to about 400°C, by means of a small tube furnace placed around the cell, and the system was pumped at high vacuum overnight. In the morning the tube furnace was removed, cooling water was flowed through the condenser,



Mercury Freezing Point Cell
Borosilicate Glass

Figure 26. Borosilicate-glass cell used to contain mercury samples for triple-point measurements.

[Two inlet tubes into the cell were essential for thorough cleaning. After cleaning, the shorter 7 mm tube was flame sealed.]



Arrangement for Filling Mercury Cell

Figure 27 Arrangement used for filling mercury cells by vacuum distillation. [The borosilicate-glass cell was baked at 400°C under high vacuum for about 16 hours; all of the mercury sample in the reservoir was then vacuum distilled into the cell; when filled, the cell was flame sealed under vacuum.]

and the power to the heating mantle around the reservoir was switched on. The system was continuously pumped at high vacuum during the distillation process. When all of the mercury was distilled into the cell, the cell was flame sealed under high vacuum. (With the stainless-steel cell, the filling tube was pinched flat near the top of the cell and then severed and sealed at the flat by arc welding under protective argon atmosphere.)

6.4 Realization of Mercury Triple Point by a Freezing Method

A suitable temperature controlled bath that could be operated unattended overnight was not immediately available for mercury freezing experiments. A vacuum-tight stainless-steel jacket (see Figure 28) was designed to control the heat transfer between the mercury cell and the Dry Ice-ethyl alcohol bath (henceforth to be referred to as the cooling or freezing bath, see Figure 29) in which the assembly was immersed. The heat transfer rate was controlled by adjusting the gas (air) pressure in the space between the cell and the jacket. Freeze durations of 14 hours or longer have been obtained when the space was continuously pumped at high vacuum.

The mercury freeze is usually prepared as follows.

1.) The mercury cell is first installed inside the stainless-steel jacket (refer to Figure 28). The copper foil (0.1 mm thick) cylinder (I) plus the paper tissue cylinder (H) help to guide the cell onto the centering stand (M). (The inside diameter of the copper foil cylinder is slightly larger than the cell so that the cylinder would not be in contact with the cell. Since the mercury supercools somewhat, it is felt that the overall heat capacity should not be increased unnecessarily. Otherwise, when the mercury recovers from the "supercool" and begins to freeze, the extra heat capacity can freeze too much mercury. The thermometer well extension (B) is sealed at (A). A vacuum valve is attached to the holder before connecting to a vacuum system.

2.) With air in the jacket space, the assembly is immersed in the cooling bath inside one of the aluminum tubes shown in Figure 29. The insides of the aluminum tubes are free of solid Dry Ice to permit ready insertion of the cell assembly. The thermometer well is filled with ethyl alcohol and a monitoring SPRT is inserted into the well.

3.) When the SPRT indicates that the mercury has cooled to a temperature near the freezing point, the jacket is evacuated. Depending upon when the evacuation is started and is complete enough to reduce the cooling rate to a small value, the sample temperature could become cold enough for the mercury to start freezing or it could become supercooled to a temperature where spontansous freezing would not occur. In borosilicate-glass cells, the mercury supercooled about 6°C; in the two type 304 stainless-steel cells, the mercury supercooled only 0.1 to 0.3°C.

4.) Whether the mercury has started to freeze or is supercooled, the monitoring SPRT is removed from the cell and inserted into an auxiliary glass tube of ethyl alcohol immersed in the cooling

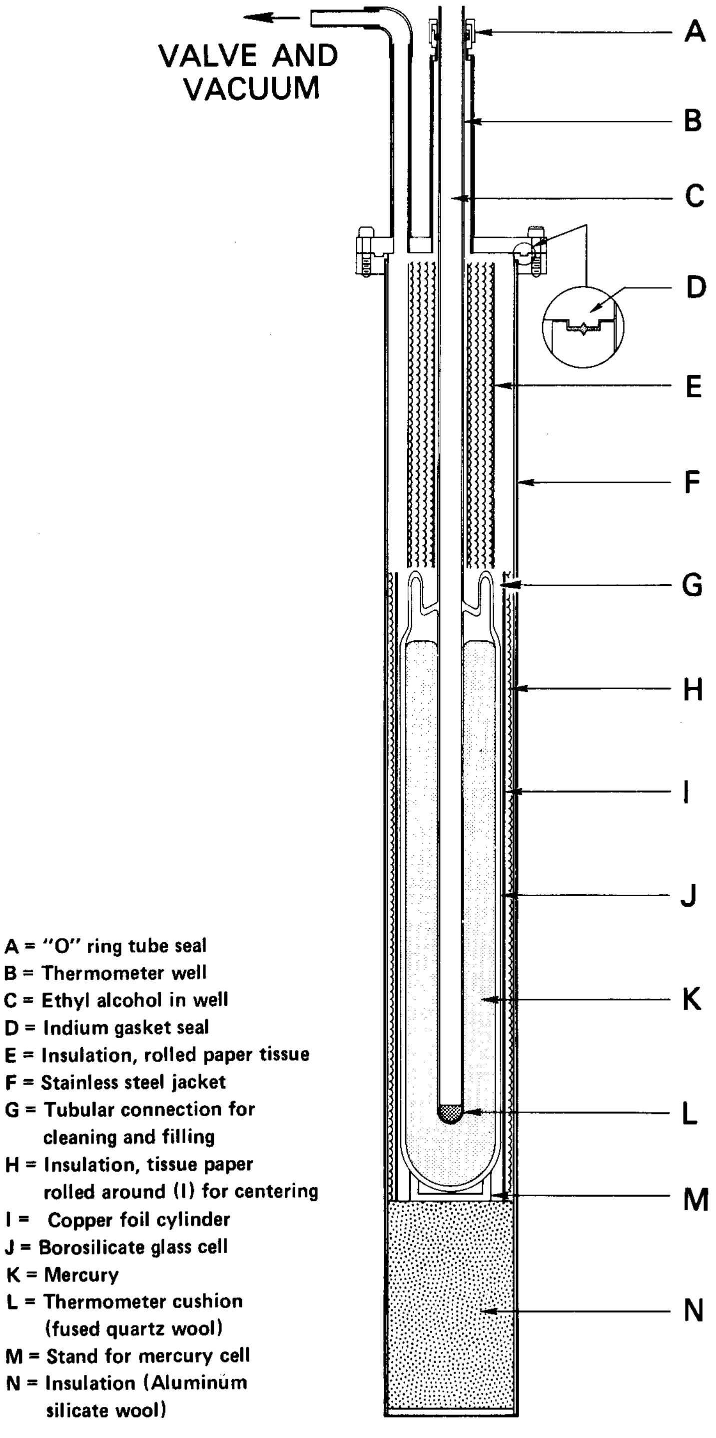
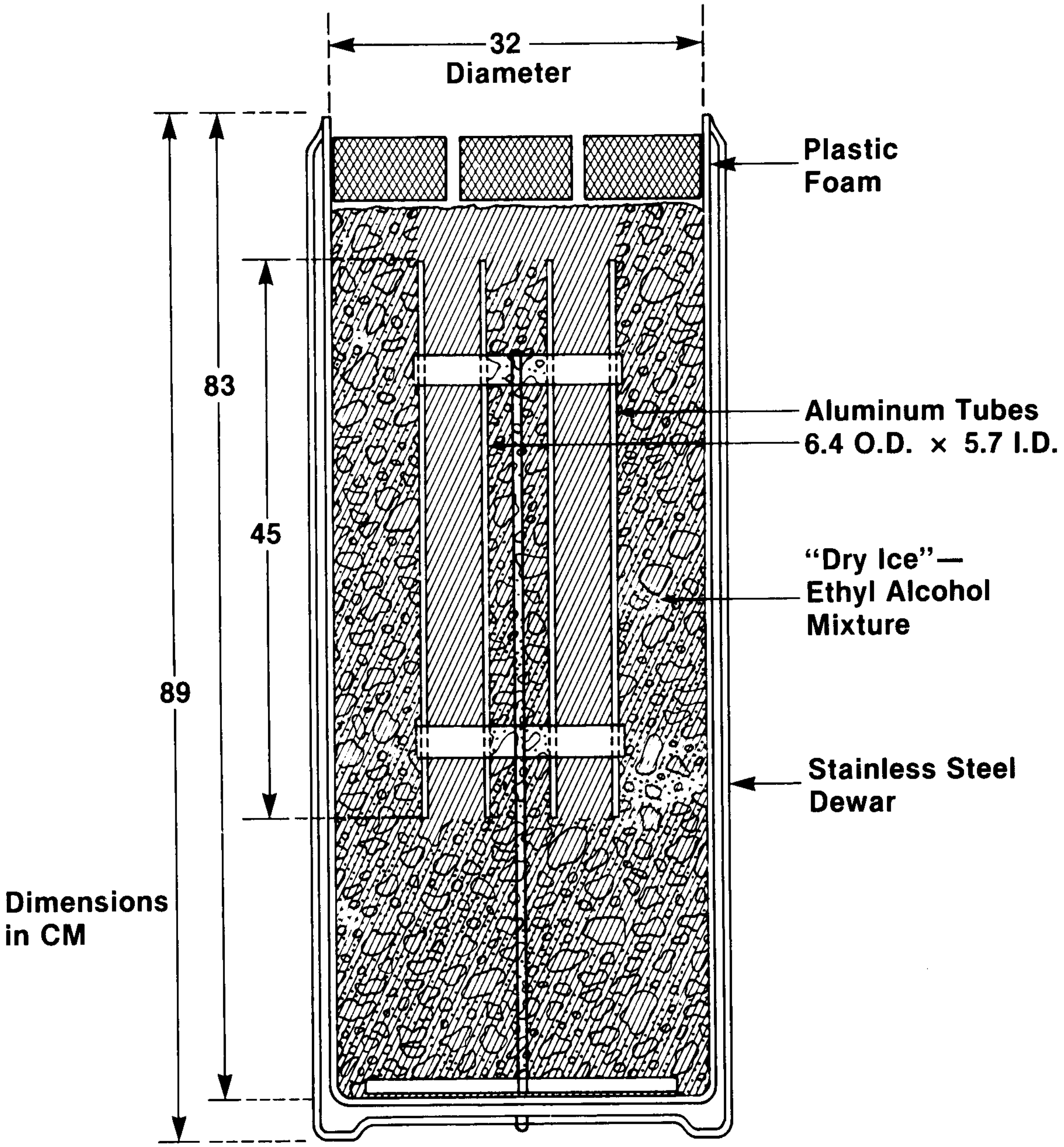


Figure 28. Mercury triple-point cell assembly.

[Cooling is started with air in the stainless-steel jacket space. When the mercury cell is adequately cooled, the space is evacuated to reduce the cooling rate. In melting experiments, the space is continuously evacuated.]



Bath for Mercury Freezing Points

Figure 29. Dry Ice - ethyl alcohol bath used in freezing experiments with mercury.

[Two mercury triple-point cell assemblies can be accommodated. The space inside the aluminum tubes is free of solid Dry Ice. Large pieces of Dry Ice surround the space around the tubes. The "flange" of the stainless-steel jacket rests on top of the aluminum tube during cooling.]

mixture. [It was felt that ethyl alcohol containing dissolved carbon dioxide may exhibit heat effects as the concentration of carbon dioxide in solution changed; hence, every effort was made to prevent any ethyl alcohol containing carbon dioxide from entering the thermometer well.]

5.) A closed-end, thin-wall stainless-steel tube containing ethyl alcohol that was precooled in the above auxiliary glass tube (see step 4) is inserted into the thermometer well of the mercury cell. [Henceforth, the auxiliary glass tube containing ethyl alcohol that is immersed in the freezing bath and used to precool the stainless-steel tube or the SPRT to the temperature of Dry Ice will be referred to as the precooling bath.]

6.) Three glass rods which had been precooled in liquid nitrogen are successively inserted into the stainless-steel tube to induce the mercury to freeze around the thermometer well. Each of the rods is allowed to remain in the stainless-steel tube from 3 to 5 min before it is removed and the next rod inserted. [The auxiliary stainless-steel freezing tube is used inside thermometer well to avoid introducing ice particles into the well from the frost-covered, liquid-nitrogen-cooled glass rods. Any ice that is introduced into the stainless-steel tube will be removed with the tube. If the auxiliary stainless-steel freezing tube is not used, the ice that is introduced into the thermometer well will slowly dissolve in the ethyl alcohol. The heat of solution of the process will be detected by the SPRT and will interfere with the mercury triple-point measurements. On the other hand, whenever the auxiliary stainless-steel tube or the SPRT is removed from the precooling bath and inserted into the thermometer well, some moisture from the air is expected to dissolve during the transit period in the ethyl alcohol that adheres to the stainless-steel tube or the SPRT sheath. However, in this case the water will be already dissolved in the ethyl alcohol; the heat effect, if detectable at all, should arise from the mixing of adhering water-ethyl alcohol solution with the ethyl alcohol that is in the thermometer well. This possible heat effect has not been distinguishable under the conditions of the experiments that have been employed.]

Figure 30 shows the results of continuous freezing of mercury as observed with an SPRT that is left undisturbed in the cell during the whole freezing process. Results from six cells are shown, two cells each of the three mercury sample source. The curves are shown displaced, in temperature, so that the shape of each freezing curve can be fully seen. Those curves with an initial higher value ("hump") are considered to be the result of heating effects associated with the dissolution of ice in the ethyl alcohol in the thermometer well. The ice was introduced when the frost-covered, liquid-nitrogen-cooled rods were inserted directly into the well. Those curves stainless-steel freezing tube was used with the liquid-nitrogen-were cooled rods to freeze mercury onto the thermometer well.

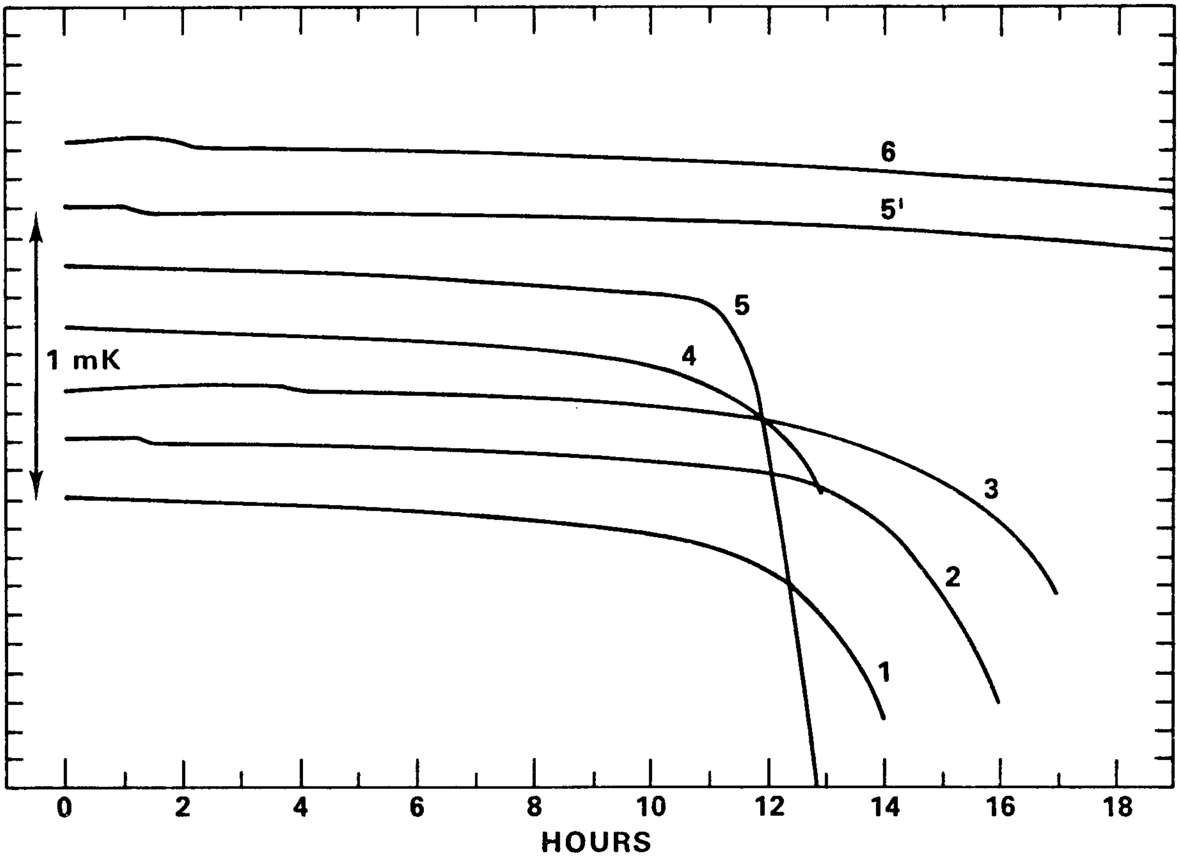


Figure 30. Freezing curves of six mercury cells.

[An a-c bridge was used in the measurements. Cells 1 and 2: density standard mercury; cells 3 and 4: SRM-743 mercury; and cells 5 and 6: Pressure Section mercury. Freezing curves were recorded approximately fifteen minutes after insertion of the SPRT in the cell. The small initial anomaly (about 0.02 mK) is attributed to the heat of solution in ethyl alcohol of small ice particles that were introduced into the thermometer well when a liquid nitrogen cooled rod was inserted directly into the thermometer well to induce an "inner freeze" around the thermometer well (see text). The anomaly was absent, when no ice was introduced. The curves are displaced vertically to show the relative temperature of individual freezing curves. The numbers identifies the cells; the prime indicates a second freeze of the cell.]

7.) After removing the third rod and the auxiliary stainless-steel freezing tube, the monitoring SPRT is removed from the precooling bath and is inserted into the thermometer well. With the induced inner freeze around the thermometer well and when the SPRT is precooled to the Dry-Ice temperature, the SPRT reaches temperature equilibrium within about 4 min (see Figure 31).

8.) After the monitoring SPRT is read, other SPRT's, after being precooled in the precooling bath, may be successively inserted into the mercury cell, for calibration. After a group of SPRT's (perhaps six) is calibrated, the triple point is checked with the monitoring SPRT; the second reading must be within ± 0.1 mK of the reading obtained before the test SPRT's were calibrated.

Figure 31 shows consecutive measurements of SPRT resistance in the same mercury freeze (or melt). After each equilibrium resistance observation, the SPRT was withdrawn from the mercury cell and placed into the precooling bath. After about two to five minutes, the SPRT was reinserted into the mercury cell. Measurement sets B and C show the SPRT warming to the equilibrium temperature. Measurement set A shows the readings obtained with a stainless-steel cell during a melting experiment. In this case, the SPRT was removed from the cell momentarily, then reinserted, so that the SPRT cools to the equilibrium temperature.

6.5 Realization of Mercury Triple Point by a Melting Method

Since the mercury samples are extremely pure the triple points obtained by freezing and by melting should yield nearly the same values. The impurity segregation during freezing should be relatively small, so that the temperatures that are observed during melting are expected to be quite close to those obtained during the freezing experiments. With less pure samples, the relatively larger impurity segregation will cause the temperatures during melting, particularly during the initial period, to be lower than those obtained in the freezing experiments. When the triple point was observed by melting immediately after observing the triple point of the mercury sample by slow freezing, where impurity segregation is expected to be relatively higher, the values differed at most by about 0.2 mK (see Figure 32, curves BS/F and BS/M). However, if the mercury had previously been frozen as rapidly as possible to minimize impurity segregation, the values of the triple point by melting would be even closer to those obtained during freezing experiment.

In preparation for the melting-point experiments, the mercury is frozen as rapidly as possible by either of two procedures. In the first procedure the cell assembly is immersed in the freezing bath. A monitoring SPRT is inserted in the thermometer well of the cell. With 1-atm pressure of air in the jacket space, the mercury is usually completely frozen within 20 to 25 min after the start of freezing. When the freezing is complete, the jacket is immediately evacuated and the cell assembly is transferred to a plastic-foam container (see Figure 33) for the melting experiments. To prolong the melting process the jacket is continuously pumped during the experiment. Under such conditions, the melting time has been about 8 to 10 hours.

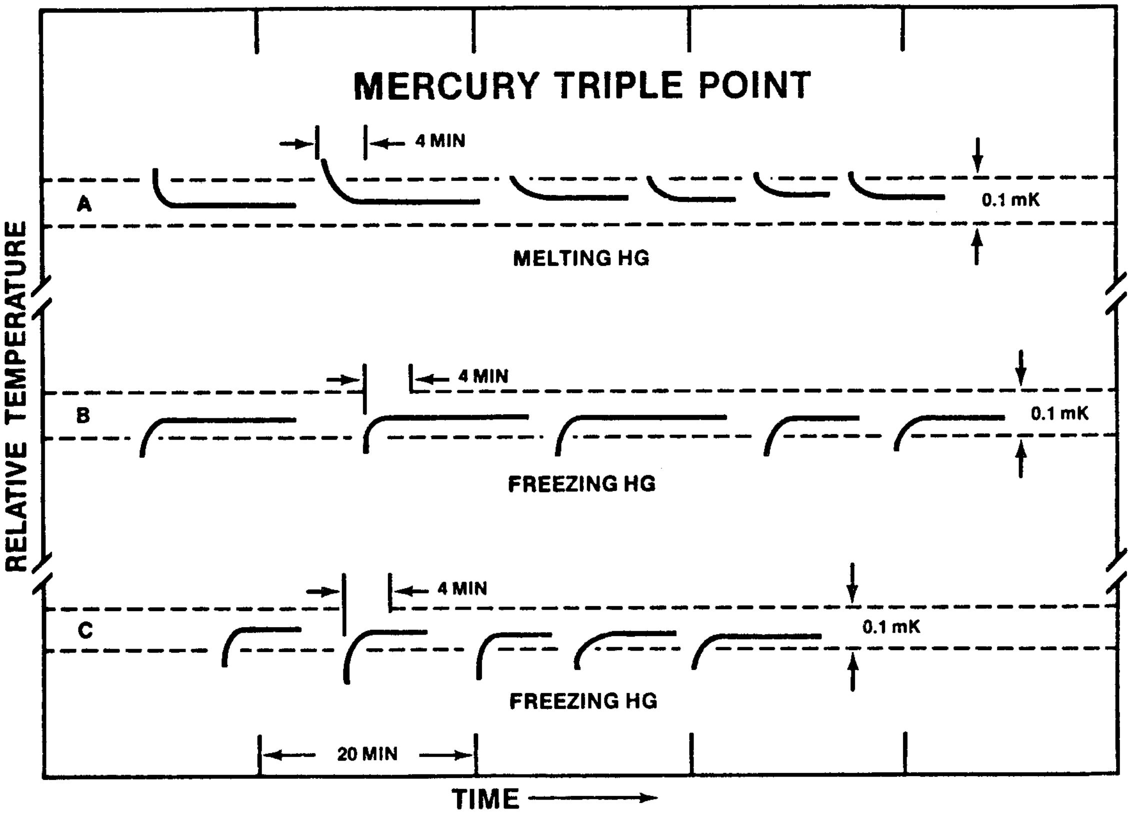


Figure 31. Consecutive measurements of the resistance of an SPRT in two mercury freezes (measurement sets B and C) and in the same mercury melt (measurement set A) [SRM-743].

[An a-c bridge was employed in the measurements. In the case of the mercury freezing experiments, following each equilibrium resistance observation, the SPRT was withdrawn from the cell and inserted into the "precooling bath" at the Dry-Ice temperature. The SPRT was then reinserted into the mercury cell. The curves show that the SPRT warmed to the cell temperature. In the case of the mercury melting experiments, following the equilibrium resistance observation, the SPRT was withdrawn completely out of the cell and then quickly reinserted into the cell. In this case, the curves show that the SPRT cooled to the cell temperature.]

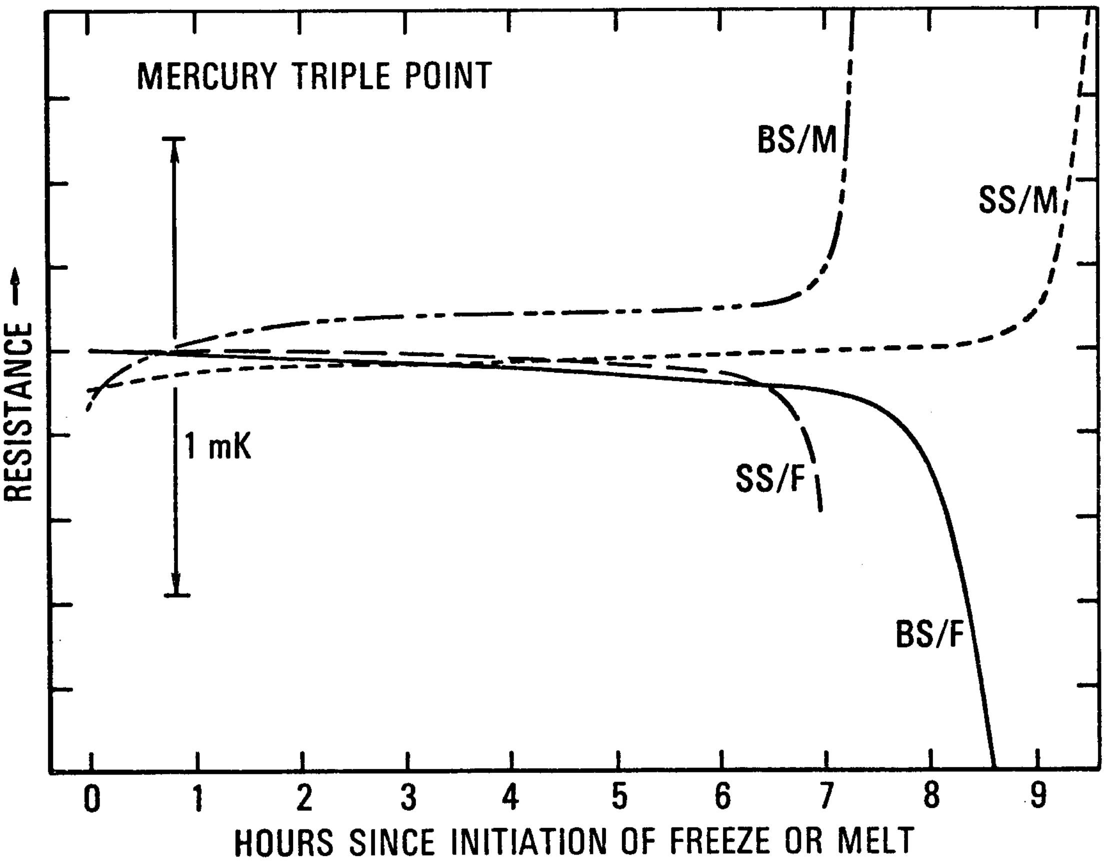


Figure 32. Freezing (F) and melting (M) curves obtained with mercury samples in borosilicate-glass (BS) and stainless-steel (SS) cells.

[An a-c bridge was used in the measurements. The melting curve (BS/M) was obtained immediately following the slow freezing-curve (BS/F) measurements. The melting curve (SS/M) was obtained after freezing the mercury with a heat pipe in the thermometer well.]

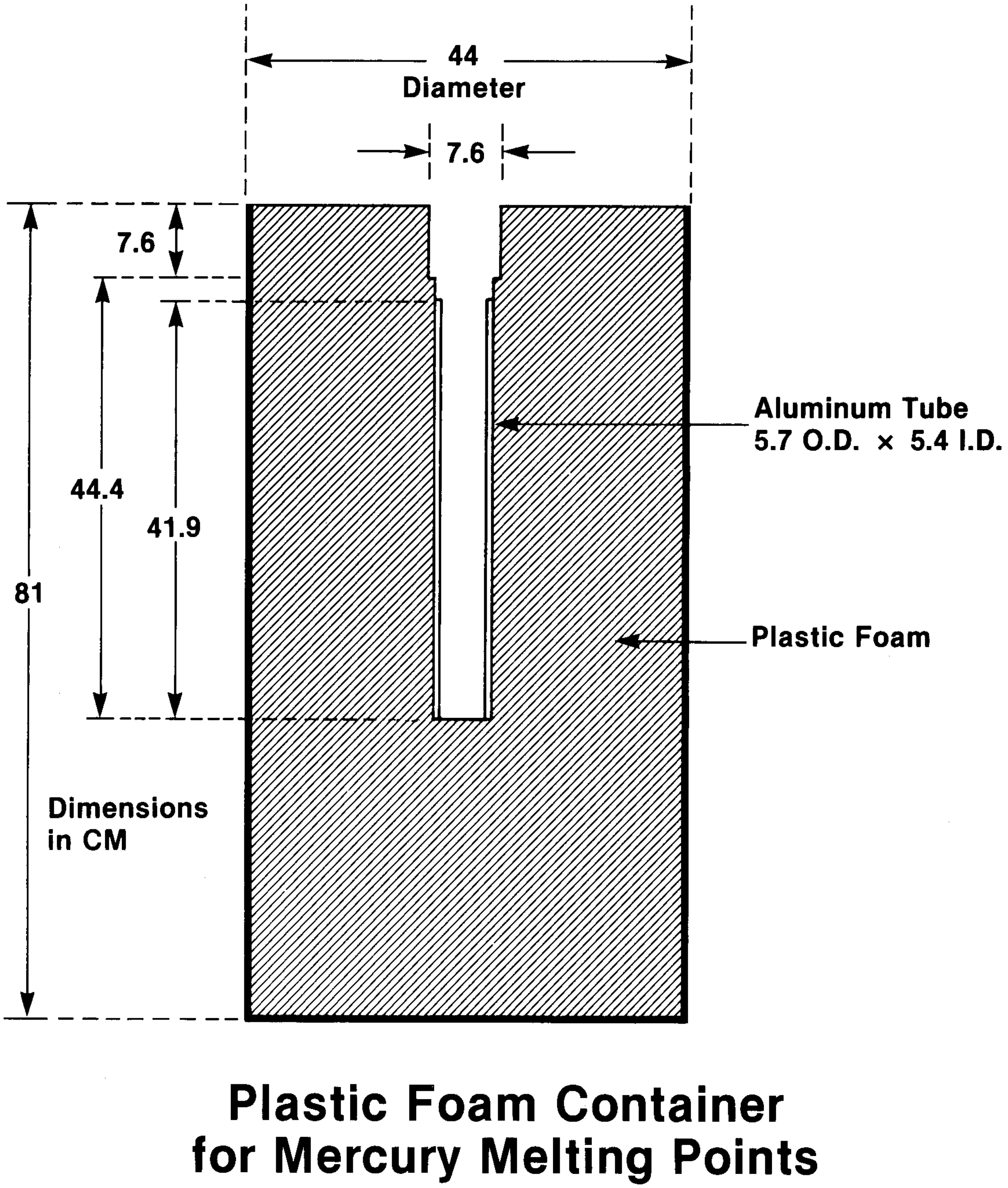


Figure 33. Plastic foam container used in melting experiments with mercury. [The stainless-steel jacket containing the mercury cell is inserted into the well of the container. The jacket space is continuously evacuated to minimize the heat transfer rate.]

In the second freezing procedure a heat pipe similar to that described by Evans and Sweger [11] is used inserted in the thermometer well of the mercury cell. As during measurements of the cell temperature, ethyl alcohol is used in the well to enhance heat transfer. The cell assembly is inserted into the plastic-foam container and the jacket space is continuously evacuated during the freezing process. The fluid in the heat pipe is difluoro-dichloromethane (CF_2Cl_2) and the coolant is Dry Ice - ethyl alcohol mixture. The mercury is usually completely frozen within about 15 to 20 min after the start of freezing. To monitor the freezing process, a thermocouple (type E) is attached to the mercury cell and brought out through a vacuum seal at the top of the stainless-steel jacket. When the thermocouple voltage indicates that the mercury sample is completely frozen, the heat-pipe cooler is removed from the thermometer well.

For both freezing procedures, the same melting technique is used to observe the triple point. The stainless-steel jacket space is pumped at high vacuum to prolong the melting time. After the frozen mercury reaches a steady-state temperature as observed with the monitoring SPRT, the number of warming rods that must be inserted into the thermometer well to just start melting is estimated from the temperature of the frozen mercury and the melting point. This estimate is based on previous melting experiments using the thermocouple indication as guide, where warming rods were successively inserted until the thermocouple indicated that the melting point was reached. (An industrial PRT, which is more sensitive, could be attached to the mercury cell instead of a thermocouple. A heater could also be attached to the cell for heating to the melting point.) After sufficient warming, a thin film of melted mercury is formed around the thermometer well placing the liquid-solid interface close to the SPRT during measurements. The triple point is first observed with the monitoring SPRT. This is followed successively with test SPRT's that have been precooled in the precooling bath. Figure 32 shows freezing and melting curves obtained with borosilicate-glass and stainless-steel mercury triple-point cells. The melting curve (BS/M) with the borosilicate-glass cell was obtained immediately after the slow-freezing experiments (BS/F). The melting curve (SS/M) with the stainless-steel cell was obtained immediately after freezing the mercury with a heat pipe inserted in the thermometer well. Figure 31 shows successive observations with the same SPRT to demonstrate the repeatability of the realization of mercury triple point during melting (see measurement set A).

7. Summary

The paper has described equipment and procedures that have been developed at the NBS to realize the freezing (or melting) points of SRM's of zinc, tin, aluminum, cadmium, and mercury. The reproducibilities of the freezing points of the purer SRM's of these metals are shown to be about ± 0.1 mK or better. The less pure SRM's can be used by similar techniques to obtain freezing points; however, the temperatures that are observed will have greater variation because of the effect of impurities (see Appendices for the certified freezing-point values of the less pure metal SRM's).

Techniques for the realization of the metal fixed points are being improved continuously. Other metals (e.g., indium, lead, bismuth, etc.) are expected to be tested in the near future.

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9. Appendices

Certificates and Analyses of Standard Reference Materials and Research Materials of Zinc, Tin, Aluminum, Cadmium, and Mercury.

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

APPENDIX A

Certificate

STANDARD REFERENCE MATERIAL 740

Zinc

Freezing Point on the International Practical Temperature Scale (1968)

419.58 °C

The temperature given above is the value assigned to the freezing point of pure zinc as one of the defining fixed points on the International Practical Temperature Scale of 1968. The fixed point is realized as the plateau temperature (or liquidus point) on the freezing curve of slowly frozen high-purity zinc.

The zinc for this standard is of exceptional purity with the total of all other elements that affect the freezing point less than one part per million. Based on samples tested, the temperature range of melting for the bulk material is not expected to exceed 0.001 degree. Plateau temperatures for samples of this material are not expected to differ from one another by more than about 0.0002 degree, and by not more than 0.001 degree from the assigned temperature.

Further information on temperature scales and metal freezing points may be found in [1] "The International Practical Temperature Scale of 1968," Metrologia, Vol. 5, p. 35 (April 1969). and [2] McLaren, E. H., "The Freezing Points of High-Purity Metals and Precision Temperature Standards" Temperature, its Measurement and Control in Science and Industry, Vol. 3, Part 1, Reinhold Publishing Corp., New York, N. Y. (1962).

The zinc metal for the preparation of this standard reference material was obtained from Cominco American Incorporated of Spokane, Washington. Evaluation of purity and homogeneity were performed in the NBS Institute for Materials Research by Robert Powell of the Cryogenic Properties of Solids Section and by Robert Alvarez and Paul Paulsen of the Spectrochemical Analysis Section. Temperature studies were performed in the NBS Institute for Basic Standards by John P. Evans of the Temperature Section.

Washington, D. C. 20234
February 19, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

SUPPLEMENTARY INFORMATION
PREPARATION, TESTING, AND HANDLING OF HIGH-PURITY ZINC FREEZING POINT MATERIAL

PREPARATION: The zinc was prepared to obtain material of the highest possible purity and homogeneity.

1. **The starting material was a carefully selected lot of electrolytic special high-grade zinc (99.99+).**

2. **Processes included vacuum distillation, zone refining, and homogenization.**

3. **Analytical control was maintained throughout the entire preparation.**

4. **The final bars (about two feet long) were individually sealed in argon filled polyethylene bags.**

TESTING: Selected samples were taken for testing which were representative of the entire lot.

1. **Testing initially was performed by optical emission and spark source mass spectroscopic procedures and by resistivity ratio measurements. As a result of this testing the material tentatively was accepted both from the homogeneity and composition standpoints.**

2. **Finally thermal analysis of selected samples was performed to determine the suitability of the material for the freezing point standard. Based on the samples tested. the temperature range of melting for the bulk material is not expected to exceed 0.001 degree, and by not more than 0.001 degree from the assigned temperature of 419.58 °C.**

HANDLING: Any handling procedures on ultra high-purity material are apt to introduce contamination. The procedures which follow were established to minimize contamination particularly with respect to the elements that could affect the freezing point measurements.

1. **The zinc bars were cut dry with a carbide tipped cutter (to form 350g bar sections) in such a way that only the carbide tip touched the zinc metal. At no time were the zinc bars touched by hand (polyethylene gloves were used), and at no time were the bars in contact with any part of the milling machine other than through the polyethylene cover.**

2. **Following cutting, the samples were acid cleaned in high-purity dilute nitric acid, rinsed with distilled water, and then air dried.**

3. **Individual samples were bagged in polyethylene and sealed.**

SHOULD ANY CUTTING OF THE SAMPLES BE REQUIRED OR SHOULD ANY CONTAMINATION BE SUSPECTED, IT IS RECOMMENDED THAT THE APPROPRIATE HANDLING PROCEDURES DESCRIBED ABOVE BE EMPLOYED JUST PRIOR TO USE.

U. S. Department of Commerce
Frederick B. Dent
Secretary
National Bureau of Standards
Richard W. Roberts, Director

APPENDIX B

National Bureau of Standards

Certificate

Standard Reference Material 43h

Zinc

Freezing Point on the International Practical Temperature Scale (1968)

419.5 °C

The freezing point of SRM 43h, 419.5 °C, is the value assigned based on the relative chemical purity with respect to all former SRM 43 standards and with respect to the highest purity zinc freezing point standard, SRM 740. It is estimated that the freezing point will not deviate from the assigned temperature by more than ± 0.1 °C.

Full details of the precautions that should be observed in freezing point determinations are given in National Bureau of Standards Circular 590, and in Metrologia 7, No. 3, 108-130 (July 1971). The International Practical Temperature Scale of 1968 is described in Metrologia 5, No. 2, 35-44 (April 1969).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
August 15, 1973

J. Paul Cali, Chief
Office of Standard Reference Materials

U. S. Department of Commerce
C. R. Smith
Secretary
National Bureau of Standards
A. V. Astin, Director

APPENDIX C

Certificate of Analysis

Standard Reference Material 683

Zinc Metal[1]

This standard of zinc metal is issued as a special research material to further both chemical and physical methods of characterization. Two other zinc metal standards are also available: SRM 682, High-Purity Zinc, and SRM 782, Intermediate-Purity Zinc. All three standards were prepared from the same starting material.

Element[2]	Recommended Value (ppm by wt.)	Range of Values Reported[3] (ppm by wt.)	Method of Analysis[4]
Lead	11.1	(9.6 – 11.3)	SSMS–ID, POL
Copper	5.9	(5.3 – 6.1)	SSMS–ID, POL
Iron	2.2	(1.7 – 3.1)	POL, SPPH
Silver	1.3	(1.0 – 1.4)	SSMS–ID, NAA
Cadmium	1.1	(1.0 – 1.2)	SSMS–ID, POL
Thallium	(0.2)[5]	(0.17 – 0.18)	SSMS–ID
Tin	(0.02)	(0.013 – 0.023)	SSMS–ID

1. The zinc is in the form of semicircular bar segments about 2 1/4 inches in diameter, 1 inch deep at mid-diameter, and 3/4 inch long.

2. In the course of analysis by neutron activation, additional elements were sought. The following elements were not detected and are reported with an estimated upper limit of concentration in parts per million by weight:

As	<(0.002)	Mn	<(0.2)	Sc	<(0.003)
Ga	<(0.002)	Mo	<(0.02)	V	<(0.005)
In	<(0.02)	Rh	<(0.3)	W	<(0.0001)

Potassium was not detected by either flame emission spectroscopy or by neutron activation at the 0.2 ppm level.

Aluminum, antimony, and sodium were detected by several techniques. The results were variable, but in no case are these elements present to a greater concentration than 3 ppm. Gold appears to be < 0.02 ppm.

3. The range of values reported is the extreme variation of the individual results reported by the methods of analysis used. The recommended value is based on considerations of the estimated systematic bias of each of the methods employed. From 7 to 13 individual determinations were made for each element certified.

4. SSMS–ID – Spark-Source Mass Spectrometry – Isotopic Dilution (R. Alvarez and P. Paulsen)
POL – Polarography (E. J. Maienthal)
SPPH – Spectrophotometry (E. R. Deardorff)
NAA – Neutron Activation Analysis (B. A. Thompson and D. A. Becker)

5. Values in parentheses are not certified since only one method of analysis was used, but are provided for additional information on the composition.

Washington, D. C. 20234
July 9, 1968

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(over)

This standard has been established to provide a homogeneous reference material for the analysis of pure zinc and analogous metals. It should also serve a useful function for the physicist and materials engineer involved in the preparation and characterization of phosphors and other solid-state compounds, where a knowledge of the purity of the starting material is important. The material was prepared by Cominco American, Inc. from a special lot of high-grade electrolytic zinc which was homogenized and cast in the form of semicircular bars. Each bar was etched, dried, and sealed in a polyethylene pouch to minimize contamination.

Extensive homogeneity testing was performed by NBS Washington and Boulder and the material was found to be satisfactory for the elements certified. The samples selected for testing were carefully chosen to represent the extreme variations that might be expected as a result of the preparation procedures. However, practical limitations precluded the testing of the number of samples from each bar that would have been required to guarantee absolute limits of homogeneity. Therefore, some inhomogeneity in the untested material is possible but not probable. The testing was performed using combinations of the following methods: optical emission and spark-source mass spectrographic analysis, polarographic analysis, flame emission and atomic absorption analysis, neutron activation analysis, and electrical measurements for residual resistivity ratios.

Although the spark-source mass spectrographic measurements indicated homogeneity with respect to microsamples, it is recommended that samples as large as possible be utilized, preferably representative of the full cross-section.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

CAUTION

Before use, it is recommended that possible surface contamination be removed by placing the sample in dilute high-purity nitric acid for about one minute, followed by rinsing in distilled water.

APPENDIX D

U. S. Department of Commerce
Peter G. Peterson
Secretary

National Bureau of Standards

Certificate

Standard Reference Material 42g

Tin

Secondary Freezing Point Standard

231.967 °C

(International Practical Temperature Scale - 1968)

The freezing point of SRM 42g, 231.967 °C, is the value determined by comparison with SRM 741, Tin Primary Freezing Point Standard (International Practical Temperature Scale–1968). The freezing point of SRM 741 is estimated to be 231.9681 °C ± 0.0007 °C. [The IPTS-68 assigned freezing point of pure tin is 231.9681 °C.]

The observed freezing points (with 25 percent in the solid phase) of three selected samples of SRM 42g, each of which weighed 1300 g, agreed within ± 0.1 mK and averaged 0.5 mK lower than the average value of eleven samples of SRM 741. (For full details of the preparation and intercomparison of the freezing points of the tin specimens, see Proceedings of the 5th Symposium on Temperature, June 1971.)

In the freezing-point experiments, the furnace surrounding the sample cell was maintained at 0.9 K below the tin point (where the total freezing time, typically about 14 hours, was dependent on the degree of super-cooling). During these experiments, the freezing points generally did not decrease by more than 0.3 mK over a period of seven hours. The standard deviation of the freezing temperatures of each sample was ± 0.05 mK from freeze to freeze (with about 25 percent in the solid phase).

Technical measurements at NBS leading to certification were performed by G. T. Furukawa, J. L. Riddle, and W. R. Bigge of the NBS Heat Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D.C. 20234
July 18, 1972

J. Paul Cali, Chief
Office of Standard Reference Materials

APPENDIX E

U. S. Department of Commerce
Frederick B. Dent
Secretary
National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards
Certificate

Standard Reference Material 741

Tin

Primary Freezing Point Standard

231.9681 °C

(International Practical Temperature Scale-1968)

The temperature given above is the value assigned to the freezing point of pure tin as one of the fixed points on the International Practical Temperature Scale of 1968 [1]. Based on chemical analyses and freezing point experiments, the freezing point of SRM 741 is estimated to be:

231.9681 ± 0.0007 °C

SRM 741 is high-purity tin, with a total of all other elements that would affect the freezing point to be about 1 ppm. The freezing points (with 25 percent in the solid phase) of eleven selected specimens of SRM 741, each of which weighed 1300 g, agreed within ± 0.1 mK. (For full details of the preparation and comparison of freezing points of tin specimens, see Proceedings of the 5th Symposium on Temperature, June 1971.)

In the freezing-point experiments, the furnace surrounding the sample-cell was maintained at 0.9 K below the tin point (where the total freezing time, typically about 14 hours, was dependent on the degree of super-cooling). During these experiments, the freezing points generally did not decrease by more than 0.1 mK over a period of seven hours. The standard deviation of the freezing temperatures of each specimen was ± 0.05 mK from freeze to freeze (with about 25 percent in the solid phase).

The tin metal for the preparation of SRM 741 was obtained from Cominco American, Inc., Spokane, Washington.

Temperature studies were performed by G. T. Furukawa, J. L. Riddle, and W. R. Bigge of the NBS Heat Division.

Evaluations of purity and homogeneity were performed in the NBS Cryogenics Division (Boulder, Colo.) by V. A. Deason, A. F. Clark, and R. L. Powell; and in the NBS Analytical Chemistry Division by C. W. Mueller, P. J. Paulsen, H. L. Rook, and P. D. LaFleur.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D.C. 20234
July 18, 1972

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

For further information of temperature scales and metal freezing points, see:

[1] The International Practical Temperature Scale of 1968, Metrologia **5**, 35 (April 1969).
[2] McLaren, E. H., The Freezing Point of High-Purity Metals and Precision Temperature Standards, Temperature, its Measurements and Control in Science and Industry, Vol. 3, Part 1, Rheinhold Publishing Corp., New York, N.Y. (1962).

SUPPLEMENTARY INFORMATION

Preparation, Testing and Handling of High-Purity Tin Freezing Point Material

PREPARATION: The tin was prepared to obtain material of the highest possible purity and homogeneity. The starting material was a carefully selected lot of refined tin (99.97). Purification processes included electrolysis, zone refining, homogenization, and degasification. Close analytical control was maintained throughout the entire preparation. The final bars (about two feet long) were individually sealed in argon-filled polyethylene bags.

TESTING: Selected samples, representative of the entire lot, were tested. The tests were initially performed by optical emission and spark source mass spectroscopic procedures and by residual resistivity ratio measurements. As a result of these tests, the material was tentatively accepted both from the homogeneity and composition standpoints. Finally, freezing point studies of selected specimens were performed to determine the suitability of the material. Based on the specimens tested, the freezing point of the lot was estimated to be within ±0.7 mK of that of 100 percent pure tin.

HANDLING: Any handling procedures on high-purity materials are apt to introduce contamination. The procedures described below were followed to minimize contamination particularly with respect to the elements that could affect the freezing point measurements.

1. The tin bars were cut dry with a carbide tipped cutter in such a way that only the carbide tip touched the tin metal. At no time were the tin bars touched by hand (polyethylene gloves were used), and at no time were the bars in contact with any part of the milling machine other than through the polyethylene cover.

2. The resulting specimens were acid cleaned by immersion in 40% HCl for one minute, and then in 40% HCl plus 10% HNO_3 for one minute. After acid cleaning, the bars were rinsed in distilled water, then in alcohol, and finally air dried.

3. Individual specimens were sealed in polyethylene bags.

SHOULD ANY CUTTING OF SRM 741 BE REQUIRED OR SHOULD ANY SURFACE CONTAMINATION BE SUSPECTED, IT IS RECOMMENDED THAT THE HANDLING AND CLEANING PROCEDURES DESCRIBED ABOVE BE EMPLOYED JUST PRIOR TO USE.

U. S. Department of Commerce
Frederick B. Dent
Secretary

National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards
Certificate
Standard Reference Material 44f
Aluminum
Freezing Point on the International Practical Temperature Scale (1968)
660.3 °C

The freezing point of SRM 44f, 660.3 °C, is the value determined on representative samples of the lot. It is estimated that the uncertainty in the NBS certified value of the freezing point does not exceed ± 0.2 °C. (The estimated uncertainty includes the imprecision and possible systematic errors of the measurement.)

The material for this standard was obtained from Cominco American, Inc., Spokane, Washington, and is a selected lot of high-purity aluminum containing less than the total of 5 ppm of impurities that would affect the freezing point. The freezing point of SRM 44f may not necessarily be the same as the freezing point of pure aluminum.

Full details of the precautions that should be observed in freezing point determinations are given in National Bureau of Standards Circular 590, and in Metrologia 7, No. 3, 108-130 (July 1971). The International Practical Temperature Scale of 1968 is described in Metrologia 5, No. 2, 35-44 (April 1969).

Technical measurements at NBS leading to certification were performed by G. T. Furukawa and J. L. Riddle of the NBS Heat Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
April 5, 1973

J. Paul Cali, Chief
Office of Standard Reference Materials

APPENDIX G

Report of Investigation

ULTRA-PURITY ALUMINUM: RM-1R & RM-1C

M. B. Kasen and R. L. Powell

Ultra-Purity Aluminum is available as a Research Material (RM) in the form of round polycrystalline rods (RM-1R) approximately 4.17 mm (0.164 in) in diameter and 2.54 cm (1 in long) and as single crystal cubes (RM-1C) approximately 1 cm (0.4 in) per side.

Applications

The polycrystalline rods provide specimens for research on the mechanical and physical properties of extremely pure aluminum; for example, in determining resistivity as a function of strain at cryogenic temperatures to facilitate design of cryogenic magnets or superconductor stabilizing elements.

The single crystal material is intended for use in studies of solid state phenomena for which both extreme purity and knowledge of crystallographic orientation are required; e.g., in studies of electron spin resonance, De Haas-Van Alphen effect, cyclotron resonance, etc., and in studies relating to the Fermi surface and the transport properties of aluminum. Both the polycrystalline rods and the single crystals are useful in studies of point and line defects and in studies of the effect of such defects on the mechanical and physical properties of metals. The materials are also well suited for use in studies of grain boundary phenomena, e.g., boundary structure, migration rates and segregation phenomena.

Material Preparation

The materials were produced from an approximately 12 mm thick slab saw cut from one side of an ingot of aluminum specially zone-refined by Cominco American, Inc. A large single crystal constituting about 2/3 of the slab was reserved for production of the cubes. The remaining material was rolled to sheets ∿0.19 inch thick for use in rod production.

Rod Production

The rods were formed by swaging at room temperature. The swaging stock was prepared by cutting square sections from the sheet and filing them to an octagonal cross section.

The octagonal sections were cleaned before the first swaging pass through a 0.176 inch diameter die, cleaned after the first pass and then swaged through a 0.167 inch die for the final pass after which they were given a final cleaning treatment.

The cleaning reagent was a solution consisting of reagent grade phosphoric acid (15 parts), sulfuric acid (5 parts) and nitric acid (1 part) (all by volume). The initial cleaning was for a total immersion time of 15 minutes in the reagent held at a temperature of 190 to 200°C. The treatment consisted of two separate 7 1/2 minute immersions. A 5 minute immersion was used after the first swaging pass and a 2 minute immersion was used after the final pass. Each immersion was in a fresh batch of cleaning reagent. Each cleaning operation was followed by a careful rinse in distilled water.

The swaged and cleaned rods were cut to length, supported in a quartz boat in an air furnace, and annealed at 450° ± 5 °C for 1 hour and then cooled to room temperature at a rate of approximately 3 °C per minute.

Following a 10 minute cleaning in the mixed acids, the cubes were supported in a quartz boat in an air furnace, annealed 10 to 15 minutes at 575 ± 5 °C, and cooled to room temperature at approximately 3 °C per minute. The latter treatment removed the damaged surface layer remaining from the grinding operation. The cubes were given a final cleaning for 20 minutes in the mixed acids.

Material Characterization

Rods

The rod material has been characterized by a measured residual resistivity at 4K and by a calculated residual resistivity ratio, $\rho 237K/\rho 4K$, at the NBS laboratories in Boulder, Colorado. Residual resistivity was determined by the eddy current decay technique in which the residual resistivity of a cylindrical rod is given by the formula [1]

$$\rho = \frac{21.7R^2 .\ 10^{-9}}{\tau} \quad \text{ohm-cm}$$

where R is the specimen radius in cm and τ is the time constant of the decay curve in seconds. From these data, the residual resistivity ratio was calculated, assuming $\rho 273K = 2.44 \times 10^{-6}$ ohm-cm. [2]

The size effect correction (ρSE) subtracted from the measured residual resistivity was determined as a function of the specimen diameter, d, by the relationship

$$\rho SE \approx \frac{(\rho \ell)_\infty}{d}$$ [3]

in which

$$(\rho \ell)_\infty \quad 0.7 \times 10^{-15} \text{ ohm m}^2.$$ [4]

TABLE I

Specimen No.	Dia. mm	τ(4K) msec	ρ4K X 10^9 ohm-cm measured	Corrected	ρ273K/ρ4K Calculated	Corrected
1	4.1763	600	0.1587	0.1409	15,470	17,310
2	4.1707	570	0.1655	0.1487	14,740	16,410
3	4.1669	545	0.1728	0.1560	14,120	15,640
4	4.1669	573	0.1644	0.1476	14,840	16,530
5	4.1709	563	0.1676	0.1508	14,650	16,180
6	4.1730	563	0.1677	0.1510	14,540	16,160
7	4.1575	550	0.1704	0.1536	14,320	15,890
8	4.1600	540	0.1738	0.1570	14,040	15,540
9	4.1661	550	0.1712	0.1544	14,250	15,810
10	4.1704	565	0.1670	0.1502	14,610	16,240

	Corrected 4K X 10^9 ohm-cm	Corrected 273K/4K
Mean Values	0.151	16,160
Standard Deviation[5]	0.0047	485
95% Confidence Interval on Mean [6]	Upper 0.1544 Lower 0.1476	Upper 16,507 Lower 15,813

The inaccuracy of a single resistivity determination is estimated to be <±3%. Material variability is slightly larger than the inaccuracy of the experimental technique.

The estimated equivalent solute in solid solution based upon the corrected residual resitivity is 0.25 ppm atomic. [7]

Cubes

The residual resistivity and the residual resistivity ratio of the cubes also was determined by the eddy current method. The resistivity of a specimen of rectangular cross section is given by [1]

$$\rho = \frac{1.27}{\tau} \; \frac{a^2 b^2}{a^2 + b^2} \; 10^{-9} \text{ ohm-cm}$$

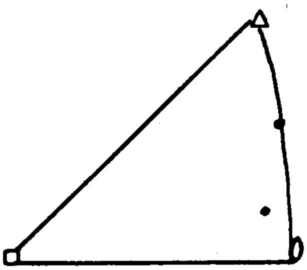
in which a and b refer to the cross sectional dimensions in cm. The above formula assumes a rod of infinite length; consequently, nine cubes were stacked in a vertical array in order to simulate the required geometry. The resulting time constant was therefore the average of the group. The following results were obtained:

$$\rho 4K = 0.1473 \times 10^{-9} \text{ ohm-cm}$$

$$\rho 273K/\rho 4K = 16{,}570.$$

This result is in agreement with the data obtained from the rod samples. (corrected for size effect).

Analysis of Laue diffraction patterns from two adjacent sides of one of the cubes revealed the normal to the cube faces to have the following crystallographic orientation:



This approximate orientation is expected to be valid for all cubes.

References

1. C. P. Bean, R. W. De Blois and L. B. Nesbitt, J. Appl. Phys. 30, 1976 (1969).
2. T. Broom, Proc. Phys. Soc. 65B, 871 (1952).
3. P. Cotti, unpublished work.
4. P. Cotti, E. M. Fryer, and J. L. Olsen, Helv. Phys. Acta. 37, 585 (1964).
5. Experimental Statistics, NBS Handbook 91, (1963), par. 1-6.
6. Ibid, par. 2-1.4.1.
7. Assuming average specific contribution to resistivity per ppm atomic to be 0.6×10^{-9} ohm-cm (cf. V. D. Arp, M. B. Kasen, and R. P. Reed, Tech. Rept. AFAPL-TR-68-87, Wright-Patterson AFB, Ohio (Feb. 1969), p.48.

Purchasers and users of these research materials are encouraged to report findings and data to:

Research Materials
Office of Standard Reference Materials
(OSRM)
National Bureau of Standards
Washington, D. C. 20234.

When a sufficient body of such information has been received, an updated Report of Investigation will be issued by the OSRM and sent to all purchasers of these materials.

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

APPENDIX H

Certificate of Analysis

Standard Reference Material 746

Cadmium-Vapor Pressure

R. C. Paule and J. Mandel

Vapor Pressure as a Function of Temperature (350-594 K)

T(K, IPTS-68)	P(atm)[a]	(1/T X 10^3) (K^{-1}, IPTS-68)	Log P(atm)[a]
350	2.49 X 10^{-11}	2.857	-10.603
400	2.97 X 10^{-9}	2.500	- 8.528
450	1.20 X 10^{-7}	2.222	- 6.922
500	2.31 X 10^{-6}	2.000	- 5.637
550	2.56 X 10^{-5}	1.818	- 4.592
594 (M. P.)	1.51 X 10^{-4}	1.684	- 3.820

---

[a] 1 atmosphere = 101,325 newtons·meter^{-2}

This SRM is available in the form of rod 6.4 mm (0.25 in) in diameter and 64 mm (2.5 in) long. The material has been determined to be homogeneous and of 99.999+ percent purity.[1] The material for this standard was supplied by Cominco American, Inc., Spokane, Washington. A specially selected lot of cadmium was further purified by distillation and zone refining, homogenized into a single lot, and processed into the final rod size.

The above vapor pressure-temperature values for solid cadmium are a composite resulting from a weighted averaging of over 200 vapor pressure-temperature measurments made by six laboratories* experienced in such measurements. The composite temperature-pressure results were obtained by using a pooled third law heat of sublimation[2] at 298 K (26660 cal/mol) and back-calculating through the third law equation:

$$\Delta H^\circ_{sub298} = T\left[\Delta\left(-\frac{G^\circ_T - H^\circ_{298}}{T}\right) - R\ln P\,(\mathrm{atm})\right] \qquad (1)$$

For the convenience of the user, the above table also includes calculated reciprocal temperatures and log pressures. The free energy functions for use in the equation are listed.[3]

The results from the six experienced laboratories have also been used to estimate statistically the uncertainties of vapor pressure measurement. The thermodynamic aspects considered in the data analysis, as well as a description of two statistical tests for use by a laboratory wishing to evaluate its results, are presented on the following pages.

The overall coordination and evaluation of data leading to certification of SRM 746 was performed by R. C. Paule and J. Mandel.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis.

Washington, D. C. 20234
August 11, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

(over)

Thermodynamics and Statistics

The individual third law heat for each data point was calculated by use of equation (1). Each laboratory's data have been recalculated at NBS using a single set of free energy functions[3] and identical calculation procedures. All temperatures have been converted to the 1968 International Practical Temperature Scale (IPTS-68).[4]

Eighteen curves from the above mentioned laboratories were also used to obtain a pooled second law heat of sublimation.[5] The second law heat for each vapor pressure-temperature curve was obtained by least-squares fitting of the A and B constants in the following equation:

$$\Delta\left(-\frac{G^\circ_T - H^\circ_{298}}{T}\right) - R \ln P\,(\mathrm{atm}) = A + \frac{B}{T} \qquad (2)$$

The slope, B, is a second law heat of sublimation at 298 K. The above calculational procedure is similar to the sigma method, and does not require the specification of a mean effective temperature.[6,7] The procedure is very convenient when the calculations, including the interpolation of free energy functions, are made by computer.

The results from the six laboratories were used to obtain a statistical estimate of the within- and the between-laboratory uncertainties exhibited by a typical in-control laboratory. It should be realized that the following uncertainty limits are not absolute or fixed with respect to time (and progress), but rather represent current average levels of uncertainty of measurement. The data from the six laboratories represent a broad cross-section of measurement techniques and include Knudsen (weight loss), torque Knudsen, and mass spectrometric methods. Temperatures were measured using several types of thermocouples. The average temperature range of the curves was 120 K and the average number of points was 13.

A laboratory wishing to evaluate its apparatus and techniques may use SRM 746 to measure a ln P vs. 1/T curve using about the same temperature range and number of data points as given above, and may then use the two statistical tests listed below. The monomer vapor species should be used in the calculations. The following Knudsen cell materials have been used satisfactorily: impervious alumina, berylia, dense graphite, iron, and iridium. Experience has shown that the orifice area should be kept smaller than 1×10^{-2} cm^2 to avoid problems of a possible non-unit evaporation coefficient. Should SRM 746 develop a slight oxide coating after extensive exposure to air, the coating may be removed by briefly rinsing the sample in 1-2 N HNO_3, followed by several distilled water rinses. After making the vapor pressure-temperature measurements, the following statistical tests should be performed.

Test I. Evaluation of the Value of the Slope

The least-squares fit of data for a single temperature-pressure curve using equation (2) should give a B value ($\Delta H^\circ_{sub\,298}$) which agrees approximately 95 percent of the time with the value 26,660 cal/mol (111,550 J/mol[(8)]) within the following limits:

$$\text{Test:} \quad \left|26{,}660 - \Delta H^\circ_{sub\,298}\right| \leq 1140 \text{ cal/mol}$$

If a laboratory prefers to least-squares fit the equation

$$R \ln P = A' + \frac{B'}{T}$$

to obtain ΔH°_T, and then adjust to ΔH°_{298} using literature $\Delta(H^\circ_T - H^\circ_{298})$ values, the above slope limits should still be approximately correct.

Test II. Evaluation of the Absolute Values of the Vapor Pressures

The average third law $\Delta H^\circ_{sub\,298}$ for a single curve, calculated as an average of individual point ΔH°_{298} values using equation (1) should agree approximately 95 percent of the time with 26,660 cal/mol (111,550 J/mol[(8)]) within the limits described below:

$$\text{Test:} \qquad \left|26{,}660 - \Delta H^\circ_{sub\,298}\right| \leqslant 420 \text{ cal/mol}$$

A further description of the evaluation of the variances for SRM 746 and their use in applications involving two or more temperature-pressure curves is given in NBS Spec. Publ. 260-21.

***List of Participating Laboratories**

Bureau of Mines, A. Landsberg
Douglas Advances Research Laboratories, D. L. Hildenbrand
Gulf General Atomic, Inc., H. G. Staley
Los Alamos Scientific Laboratory, C. C. Herrick and R. C. Feber
Marquette University, T. C. Ehlert
National Bureau of Standards, E. R. Plante and A. B. Sessoms
Sandia Corporation, D. A. Northrop

Footnotes

[1] The following methods were used in the homogeneity testing and purity evaluations:
Linear Electron Accelerator (G. J. Lutz)
Optical Emission Spectroscopy (Cominco American, Inc., Spokane, Washington - J. G. Frettingham)
Residual Resistivity Ratio, R_{273K}/R_{4K} (V. A. Deason and R. L. Powell)
Spark-Source Mass Spectrometry (C. W. Mueller and P. J. Paulsen).

[2] The third law $\Delta H^\circ_{sub\,298} = 26.660 \pm 150$ cal/mol (111,550 ± 630 J/mol). The ± uncertainty value represents two standard error limits of the pooled value. These limits tacitly assume the error in the free energy functions is negligible relative to the error in the heat of sublimation. This is believed to be the case.

[3]

Temperature K,(IPTS-68)	Condensed phase[b] $-\frac{G^\circ_T - H^\circ_{298}}{T}$ $\mathrm{cal \cdot mol^{-1} \cdot deg^{-1}}$	Gas phase $-\frac{G^\circ_T - H^\circ_{298}}{T}$ $\mathrm{cal \cdot mol^{-1} \cdot deg^{-1}}$
298.15	12.38	40.065
350	12.51	40.164
400	12.63	40.260
450	12.87	40.444
500	13.10	40.628
550	13.36	40.820
594 (M.P.)	13.61	41.011

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[b] Converted to IPTS-68[4] using data of Hultgren, R., Orr, R. L., and Kelley, K. K., loose-leaf supplement to Selected Values of Thermodynamic Properties of Metals and Alloys (Sept. 1966). Conversions were made to IPTS-68 using equations given by Douglas, T. B., J. Res. NBS, 73A, 451-69 (1969).

[4] The International Practical Temperature Scale of 1968, Metrologia 5, 35-49 (1969).

[5] The second law $\Delta H^{o}_{sub\,298}$ = 26,610 ± 380 cal/mol (111,340 ± 1600 J/mol). The ± uncertainty represents two standard error limits of the pooled value. The pooled second law and third law heats[2] are in excellent agreement. The pooled third law heat, however, is believed to be more accurate and has therefore been used in the calculation of vapor pressures and as the "best value" in the statistical tests.

[6] Horton, W. S., J. Res. NBS, 70A, 533-9 (1966).

[7] Cubicciotti, D., J. Phys. Chem., 70, 2410-3 (1966).

[8] 1 calorie = 4.1840 joules.

U.S. Department of Commerce
Elliot L. Richardson,
Secretary

National Bureau of Standards
Ernest Ambler, Acting Director

National Bureau of Standards
Certificate
Standard Reference Material 743
Mercury

Triple Point on the
International Practical Temperature Scale (1968)

−38.841 °C

This Standard Reference Material is recommended for calibrating temperature measuring devices. The temperature given above is based on the experimental comparison of slowly freezing mercury (14 hour freeze) in four sealed cells which were free of any gas. Two of these cells were prepared by combining seven ampoules of SRM 743 and two contained the high purity NBS Density Standard Mercury. The triple point temperatures of all four cells were found to agree within 0.1 mK.

The absolute value of the triple point temperature given above is based on measurements with one of the NBS Density Standard mercury cells and five platinum resistance thermometers calibrated in terms of the IPTS-68. Twelve observations were made with the thermometers in two freezes. The standard deviation of these observations is 0.1 mK.

The calculated effect of pressure on the freezing point of mercury is +5.4 mK per atm. Although temperature measurements are more precise and convenient with sealed, gas-free mercury cells, for those who prefer to employ cells open to the ambient pressure the freezing point at 1 atm pressure is estimated to be −38.836 °C. *Since the fixed point is below ambient temperature, precautions should be taken to avoid condensation of moisture on the mercury sample.*

Technical measurements at NBS leading to certification were performed by G. T. Furukawa, J. L. Riddle, and W. R. Bigge of the NBS Heat Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. E. Michaelis and R. K. Kirby.

Washington, D.C. 20234
April 22, 1976

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

SUPPLEMENTARY INFORMATION

The freezing point of mercury is one of the secondary reference points for the IPTS-68. The experimentally realized value given in this certificate is the same as that adopted by the Comité International des Poids et Mesures. For further information of temperature scales and metal freezing points, see The International Practical Temperature Scale of 1968, Metrologia 5, 35 (April 1969) and McLaren, E. H., The Freezing Point of High-Purity Metals and Precision Temperature Standards, Temperature, its Measurements and Control in Science and Industry, Vol. 3, Part 1, Rheinhold Publishing Corp., New York, N. Y. (1962).

The mercury for this standard is of exceptional purity with the total of other elements estimated to be less than 20 parts per billion (ng/g) by emission spectrographic analysis. This mercury was obtained from Cominco American, Inc., Spokane, Washington. SRM 743 is packaged in argon-filled soft-glass ampoules and weighs about 680 g (50 ml).