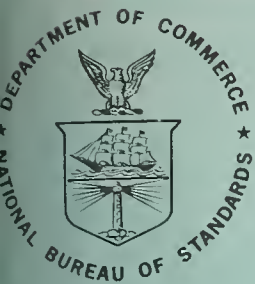


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# NBS SPECIAL PUBLICATION 260-56

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

*Standard Reference Materials:*

**STANDARD THERMOCOUPLE MATERIAL, Pt-67:  
SRM-1967**

60-56

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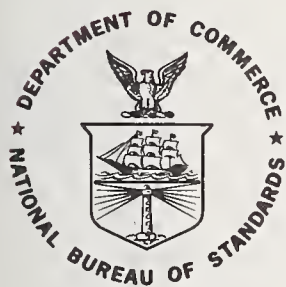
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## Standard Reference Materials:

### STANDARD THERMOCOUPLE MATERIAL, Pt-67: SRM-1967

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Industry-wide standardization of thermocouple wire depends in part on thermoelectric comparisons of commercial wires to a standard. In this paper we describe a thermoelectric standard, designated Pt-67, which is available in wire form as a Standard Reference Material (SRM 1967). High purity platinum meets the requirements of a thermoelectric reference material for temperatures from 77K (-197 °C) up to 2040K (1767 °C). Thermoelectric voltages, residual resistance ratios, temperature coefficients of resistance, and chemical composition are reported for a high purity, highly characterized lot of platinum that has been developed as a thermoelectric standard, Pt-67. A review of the historical development of the material is followed by characterization data on the material and descriptions of the cryogenic and high temperature apparatus. The important effects of impurities are also described. Recommendations and precautions for usage of the reference material conclude the discussion.

Key words: Chemical composition; effects of imperfections; high purity platinum; high temperature thermoelectric measurements; low temperature thermoelectric measurements; platinum; Pt 67; residual resistivity ratio; Standard Reference Material; temperature coefficient of resistors; thermocouple; thermoelectric standard; thermoelectric voltage.

## 1. INTRODUCTION

The ability to standardize thermocouple wires depends in part on the availability of a reliable Standard Reference Material (SRM). In addition, commercial thermocouple materials must be well characterized if excessive manufacturer-to-manufacturer, batch-to-batch, or spool-to-spool variations are to be avoided. Because of the difficulty of accurately characterizing thermocouple wires (especially base-metal alloys) in terms of composition, they must be controlled primarily by direct thermoelectric measurements. If these direct thermoelectric measurements are made with respect to a SRM which, in turn, is compared to standard reference data, then industry-wide uniformity is possible. The first step of this program, to experimentally establish such standard reference data, has been completed at cryogenic temperatures by Sparks et al. [1] and at high temperatures by Powell, et al. [2]. The next step, the establishment of a SRM, is described in this Special Publication.

The electrical characteristics of high purity platinum have been well established primarily because of platinum's extensive use in interpolating thermometers for measuring temperatures on the international temperature scales of ITS-27, IPTS-48, and IPTS-68. The platinum resistance thermometer is used from 13.81K (-259.34 °C) to 630.74 °C and the Pt-10% Rh vs Pt thermocouple is specified for higher temperatures from 630.74 to 1064.43 °C. Platinum is used by thermocouple wire manufacturers for production control of commercial thermocouples and by standards laboratories for calibrations because of its fundamental standing in the temperature scales and because it is relatively easy to obtain as reproducible, high-purity, well-characterized material.

Pure platinum and three alloys of platinum with rhodium are commonly used for high temperature thermocouple thermometry. The three standardized combinations are: (1) Platinum - 10% rhodium versus platinum (Type S), (2) platinum - 13% rhodium versus platinum (Type R), and (3) platinum - 30% rhodium versus platinum - 6% rhodium (Type B). (It is conventional in thermocouple thermometry to name the positive thermoelement first in specifying thermocouple combinations.) Usually only pure platinum and the Type S combination are used as reference materials for thermocouple calibrations at temperatures above 0 °C.

The platinum - 10% rhodium thermocouple was developed and tested by Le Chatelier almost a century ago. Because of his pioneer work, this type of thermocouple was often referred to as the Le Chatelier couple. In this country the ASTM E-20 and ISA-C96 standards for this thermocouple type were formerly taken from NBS Circular 561 by Shenker et al. [3]. The reference tables given in NBS Circular 561 were based on functions given by Roeser and Wensel [4] in 1933, as revised to conform with IPTS-48. In Great Britain the British Standards Institution Table BS 1826 for this thermocouple type was based on the research by Barber [5] in 1950. There were considerable differences between the American and British reference tables because of small differences in rhodium content, in amount of iron impurities, in purity of platinum, and in realizations of the temperature scales.

For many industrial applications, other noble metal thermocouples, Types R and B described above, have preferable characteristics and have replaced the Type S platinum - 10% rhodium vs platinum thermocouple. However, Type S thermocouples remain the standard for determining temperatures between 630.74 °C and the freezing point of gold (1064.43 °C). The official CIPM article (as amended in 1975) [6] details the temperature scale definition in this range and includes specifications on the limits of the thermocouple voltage. The other fixed point used for determining the constants in the specified quadratic interpolation formula of the thermoelectric voltage is the freezing point of silver, 961.93 °C. The primary and secondary fixed points of the IPTS-68 in the temperature range suitable for platinum reference thermoelements are given in tables 1 and 2, respectively. Modern methods of realizing those fixed points were reviewed during the Fifth Symposium on Temperature in 1971 [7].

TABLE 1 *Defining fixed points of the IPTS-68<sup>a</sup>*

Equilibrium state	Assigned value of International Practical Temperature	
	$T_{68}$ (K)	$t_{68}$ (°C)
Equilibrium between the liquid and vapor phases of oxygen (boiling point of oxygen)	90.188	-182.962
Equilibrium between the solid, liquid and vapor phases of water (triple point of water) <sup>c</sup>	273.16	0.01
Equilibrium between the liquid and vapor phases of water (boiling point of water) <sup>b, c</sup>	373.15	100
Equilibrium between the solid and liquid phases of zinc (freezing point of zinc)	692.73	419.58
Equilibrium between the solid and liquid phases of silver (freezing point of silver)	1235.08	961.93
Equilibrium between the solid and liquid phases of gold (freezing point of gold)	1337.58	1064.43

<sup>a</sup>Entries are limited to those suitable for use with platinum reference thermoelements. The assigned values of temperature are for equilibrium states at a pressure  $p_0 = 1$  standard atmosphere ( $101\,325\text{ N/m}^2$ ). In the realization of the fixed points small departures from the assigned temperatures will occur as a result of the differing immersion depths of thermometers or the failure to realize the required pressure exactly. If due allowance is made for these small temperature differences, they will not affect the accuracy of realization of the Scale. The magnitudes of these differences are given in section III of the original article by CIPM (6).

<sup>b</sup>The equilibrium state between the solid and liquid phases of tin (freezing point of tin) has the assigned value of  $t_{68} = 231.9681\text{ °C}$  and may be used as an alternative to the boiling point of water.

<sup>c</sup>The water used should have the isotopic composition of ocean water, see section III, 4, of the original article by CIPM (6).

TABLE 2. Secondary reference points of the IPTS-68

Equilibrium state	International Practical Temperature	
	$T_{68}$ (K)	$t_{68}$ (°C)
Equilibrium between the liquid and vapor phases of nitrogen (boiling point of nitrogen)	77.344	-195.806
$\lg \frac{p}{p_0} = A + \frac{B}{T_{68}} + C \lg \frac{T_{68}}{T_0} + DT_{68} + ET_{68}^2 \quad (25)$ <p> <math>A = 5.893\,271</math>, <math>B = -403.960\,46\text{K}</math>, <math>C = -2.3668</math>, <math>D = -0.014\,281\,5\text{K}^{-1}</math>,  <math>E = 72.5872 \times 10^{-6}\text{K}^{-2}</math>, <math>T_0 = 77.344</math>,                      for the temperature range from 63.146 K to 84 K.                 </p>		
Equilibrium between the liquid and vapor phases of oxygen		
$\lg \frac{p}{p_0} = A + \frac{B}{T_{68}} + C \lg \frac{T_{68}}{T_0} + DT_{68} + ET_{68}^2 \quad (26)$ <p> <math>A = 5.961\,546</math>, <math>B = -467.455\,76\text{K}</math>, <math>C = -1.664\,512</math>, <math>D = -0.013\,213\,01\text{K}^{-1}</math>,  <math>E = 50.8041 \times 10^{-6}\text{K}^{-2}</math>, <math>T_0 = 90.188\text{K}</math>                      for the temperature range from 54.361 K to 94 K.                 </p>		
Equilibrium between the solid and vapor phases of carbon dioxide (sublimation point of carbon dioxide)	194.674	-78.476
$T_{68} = \left[ 194.674 + 12.264 \left( \frac{p}{p_0} - 1 \right) - 9.15 \left( \frac{p}{p_0} - 1 \right)^2 \right] \text{K} \quad (27)$ <p>for the temperature range from 194 K to 195 K.</p>		
Equilibrium between the solid and liquid phases of mercury (freezing point of mercury) <sup>b</sup>	234.314	-38.836
Equilibrium between ice and air-saturated water (ice point)	273.15	0
Equilibrium between the solid, liquid and vapor phases of phenoxybenzene (diphenyl ether) (triple point of phenoxybenzene)	300.02	26.87
Equilibrium between the solid, liquid and vapor phases of benzoic acid (triple point of benzoic acid)	395.52	122.37
Equilibrium between the solid and liquid phases of indium (freezing point of indium) <sup>b</sup>	429.784	156.634
Equilibrium between the solid and liquid phases of bismuth (freezing point of bismuth) <sup>b</sup>	544.592	271.442
Equilibrium between the solid and liquid phases of cadmium (freezing point of cadmium) <sup>b</sup>	594.258	321.108
Equilibrium between the solid and liquid phases of lead (freezing point of lead) <sup>b</sup>	600.652	327.502
Equilibrium between the liquid and vapor phases of mercury (boiling point of mercury)	629.81	356.66
$t_{68} = \left[ 356.66 + 55.552 \left( \frac{p}{p_0} - 1 \right) - 23.03 \left( \frac{p}{p_0} - 1 \right)^2 + 14.0 \left( \frac{p}{p_0} - 1 \right)^3 \right] ^\circ \text{C} \quad (28)$ <p>for <math>p = 90 \times 10^3 \text{ N/m}^2</math> to <math>104 \times 10^3 \text{ N/m}^2</math>.</p>		
Equilibrium between the liquid and vapor phases of sulphur (boiling point of sulphur)	717.824	444.674
$t_{68} = \left[ 444.674 + 69.010 \left( \frac{p}{p_0} - 1 \right) - 27.48 \left( \frac{p}{p_0} - 1 \right)^2 + 19.14 \left( \frac{p}{p_0} - 1 \right)^3 \right] ^\circ \text{C} \quad (29)$ <p>for <math>p = 90 \times 10^3 \text{ N/m}^2</math> to <math>104 \times 10^3 \text{ N/m}^2</math>.</p>		
Equilibrium between the solid and liquid phases of the copper-aluminum eutectic	821.41	548.26
Equilibrium between the solid and liquid phases of antimony (freezing point of antimony) <sup>b</sup>	903.905	630.755
Equilibrium between the solid and liquid phases of aluminum (freezing point of aluminum)	933.61	660.46
Equilibrium between the solid and liquid phases of copper (freezing point of copper)	1358.03	1084.88
Equilibrium between the solid and liquid phases of nickel (freezing point of nickel)	1728	1455
Equilibrium between the solid and liquid phases of cobalt (freezing point of cobalt)	1768	1495
Equilibrium between the solid and liquid phases of palladium (freezing point of palladium)	1827	1554

<sup>a</sup>Entries are limited to those suitable for use with platinum reference thermoelements. The assigned values of temperature are for equilibrium states at a pressure  $p_0 = 1$  standard atmosphere ( $101\,325 \text{ N/m}^2$ ). In the realization of the fixed points small departures from the assigned temperatures will occur as a result of the differing immersion depths of thermometers or the failure to realize the required pressure exactly. If due allowance is made for these small temperature differences, they will not affect the accuracy of realization of the Scale. The magnitudes of these differences are given in section III of the original article by CIPM (6).

<sup>b</sup>See the original article by CIPM (6) for the effect of pressure variations on these freezing points.

Because of the differences between the British and American standards for Type S thermocouples noted above, an international program was begun several years ago to rectify the unsatisfactory disagreements and to establish a common set of standard reference tables. Unfortunately the highest purity platinum was not used as the common negative reference material for that program, so a small correction must be applied to values for Type S thermocouples to reference them to the Pt-67 wire described in this Special Publication. However, the correction is automatically accounted for whenever any positive or negative thermoelement is calibrated directly, or indirectly, against the standard platinum described in this Special Publication. The program involved cooperation of three national laboratories--the National Bureau of Standards (USA), the National Physical Laboratory (UK), and the National Research Council (Canada)--and seven manufacturers in Great Britain and the United States. The thoroughly documented experimental details have been published by Bedford et al. [8] and tables and functions have also been published by Powell et al. [2].

Pt-67 (or SRM 1967) is the designation for the new platinum thermoelectric reference standard material that is maintained by the Office of Standard Reference Materials. It replaces the former standard, Pt-27, which was used from 1922 up until January, 1973. A history of Pt-27 was given by Wickers [9]. Pt-67 is a selected, highly-homogeneous, portion of the chemical composition standard, SRM 680, that was set aside to be developed as the thermoelectric standard. The historical development of Pt-67 will be described in the next section. It should be noted that Pt-27 stands for a batch number and Pt-67 stands for a date of preparation. Characterization of this reference material is described in section 3. The low temperature and high temperature thermoelectric measurements are briefly discussed in sections 4 and 5. The important effects of impurities are given in section 6. The last section, 7, includes recommendations for proper usage of this reference material, Pt-67.

At temperatures below about 50K, the thermoelectric power of platinum becomes strongly dependent on trace impurities. Thus platinum is not recommended for standard reference thermoelectric measurements below liquid nitrogen temperatures (77K). An Ag-Au alloy, SRM 733, has been established for use to 4K [10]. The present paper describes the work which has been done to certify and characterize high purity platinum for use as a thermocouple reference material between 77K and 2040K (1767 °C).

## 2. HISTORICAL DEVELOPMENT

The predecessor of Pt-67 was Pt-27. The early development of the latter was described by Wickers [9]. Early in 1922 a trial melt of platinum, numbered as 27, was found to be thermoelectrically negative to all previous specimens, and therefore by inference, to be more pure. (Note that Pt-27 refers to a batch number, but Pt-67 refers to a date.) Unfortunately, that trial melt only provided about 1 meter of wire for thermoelectric calibrations. Over the years, it was consumed and other

batches of wire were used, though the reference values were still referred to Pt-27. Gradually the apparent value of thermoelectric voltage drifted until it was arbitrarily, by decree, revised back toward a value more representative of highest purity material. A precise history of the original material and its successors is difficult to trace, but in 1949 R. J. Corruccini reviewed the status of Pt-27 and recorded his comments in a laboratory notebook [11]. The situation was obviously undesirable for a national standard, and new research on the preparation and characterization of high purity platinum was begun some 10 years later.

Representatives of major platinum refiners were aware of the need for reference material that was more pure and better characterized than the earlier Pt-27. In fact, improved industrial and chemical methods allowed the preparation and widespread usage of considerably better platinum wire. On December 14, 1959, representatives of J. Bishop & Co., Sigmund Cohn Corp.; Johnson, Matthey Co., Inc; and Engelhard Industries, Inc. met in the offices of Johnson Matthey & Co. in New York, to plan a joint cooperative test program on high purity platinum [12]. A follow-up meeting was held on August 19, 1960, at Engelhard Ind., Inc. in New Jersey. Soon thereafter members of the National Bureau of Standards actively entered the program. On September 1, 1960, a conference was held at the Van Ness Street campus of the National Bureau of Standards in Washington, D.C. That meeting was attended by NBS and industry representatives, Mr. J. F. Swindells of NBS presiding. Other NBS staff included F. R. Caldwell, J. P. Evans, R. Gilchrist, W. F. Roeser, B. F. Scribner, and E. Wickers. H. J. Albert, H. C. Anderson, Arnold J. Lincoln, and E. Zysk represented Engelhard Ind.; John Cochrane represented Johnson, Matthey & Co.; and B. Brenner represented Sigmund Cohn Corp. At that meeting it was agreed that the manufacturers would prepare a high purity lot of material and would characterize it as well as they could. Other chemical and physical characterization tests, in particular the high temperature thermoelectric measurements, would be simultaneously carried out at the National Bureau of Standards. Later R. E. Honig of the RCA Laboratories joined the program to provide mass spectroscopic analyses.

After considerable effort by many individuals and organizations, the material was finally prepared and characterized and then certified as a Standard Reference Material (SRM 680) on December 28, 1967. The material for SRM 680 was prepared at Sigmund Cohn by induction melting of high purity platinum sponge in a zirconium silicate crucible, and by casting into a platinum-lined, water-cooled copper mold. The ingot was trimmed, swaged, and drawn into wire using the utmost precautions to minimize contamination. The best specimens, based on resistivity measurements, from that lot were selected as thermoelectric standards and were distributed to several national standardizing laboratories. R. E. Michaelis of the OSRM suggested that because of the certification date, the platinum should become known as Pt-67. A select portion of the chemical standard, SRM 680, has now become certified as a thermophysical standard SRM 1967.



Cooperating with the National Bureau of Standards in this extensive analytical program were the following American and British manufacturers and laboratories: Matthey Bishop, Inc.; Sigmund Cohn Corp.; Engelhard Industries, Inc.; Johnson, Matthey Co., Ltd.; and RCA Laboratories.

### 3. MATERIAL CHARACTERIZATIONS

A high-purity lot of platinum, designated SRM 680 has received extensive characterization under the direction of the Office of Standard Reference Materials (OSRM), National Bureau of Standards. The material for Pt-67 was selected from SRM 680 platinum. SRM 680 platinum was prepared as described in the previous section.

This lot of platinum wire, SRM 680, was found satisfactory with respect to homogeneity and was subsequently certified for chemical composition. The chemical composition of Pt-67, SRM 1967, is given in table 3 where the data are the recommended values taken from the previous chemical certificate of analysis for SRM 680. The elemental analyses were made by the following analytical methods: optical emission spectrography, spark source mass spectrography (with isotopic dilution), polarography, spectrophotometry, activation analysis, and vacuum fusion.

The temperature coefficient of electrical resistance between 0 and 100 °C is commonly used as an indicator of the quality of platinum used in thermometry. The alpha coefficient is defined by:

$$\alpha = \frac{R(100\text{ }^{\circ}\text{C}) - R(0\text{ }^{\circ}\text{C})}{R(0\text{ }^{\circ}\text{C})}$$

The IPTS-68 [6] requires an alpha coefficient of  $3.925 \times 10^{-3}/^{\circ}\text{C}$  or higher for platinum used as an interpolating thermometer. Two specimens from the lot of Pt-67 wire were tested by each of four cooperating laboratories (National Bureau of Standards, Engelhard, Johnson Matthey, and Sigmund Cohn) and the values reported for the temperature coefficient of resistance,  $\alpha$ , ranged from 3.926 to  $3.9275 \times 10^{-3}\text{K}^{-1}$ . The average value for ten determinations was  $3.9269 (^{\circ}\pm 0.0011) \times 10^{-3}\text{K}^{-1}$  where the indicated uncertainty is the  $2\sigma$  value.

Each of the four cooperating laboratories listed above also determined the thermoelectric voltage of two specimens of Pt-67 against representative specimens that were descendants of the former standard, Pt-27. For measuring junction temperatures of 1200 °C and reference junctions at 0 °C, values of -9 and -10 microvolts were reported. (Note that many current comparisons are made at 1100 °C.) As could be expected from its greater purity and lack of iron and rhodium impurities, Pt-67 is thermoelectrically negative with respect to Pt-27. The value determined by the National Bureau of Standards, -9 microvolts, is used as a standard correction. For a reference junction at 0 °C, thermoelectric voltage versus temperature relationship of Pt-67 with respect to Pt-27 can be approximated by:

Table 3. Chemical Composition of Pt-67, SRM 1967<sup>1</sup>

Element <sup>2</sup>	Recommended Value Concentration in Parts Per Million by Weight	Range of Values Reported <sup>3</sup>
Copper	0.1	( 0.087 - <1 )
Silver	<0.1	( < 0.06 - <1 )
Palladium	0.2	( < 0.1 - <1 )
Lead	<1	( 0.6 - 3 )
Iron	0.7	( 0.6 - 2.6 )
Nickel	<1	( 0.3 - <1 )
Gold	<1	( < 0.1 - 8 )
Magnesium	<1	( < 0.05 - 2 )
Zirconium	<0.1	( < 0.03 - 0.3 )
Rhodium	<0.2	( 0.09 - <1 )
Iridium	<0.01	( 0.007 - 0.01 )
Oxygen	4	( 3.2 - 5.2 )*
Platinum	(remainder - 99.999 +%)	

\* Range from one laboratory only.

1. This is the same chemical composition that was certified for SRM 680, High-Purity Platinum, December 28, 1967.
2. Other elements are also contained in the standards; some of them such as Al, Ca, Na, Si, and Sn may be certified at a later date.
3. The values listed are based on a consideration of the analytical methods and results reported by cooperating laboratories. For all elements in SRM 1967, either because a single method was used or because of lack of agreement among methods, no estimate of accuracy can be made at this time.

$$\Delta E_{67-27} = -7.5 \times 10^{-3} t_{68}$$

where  $\Delta E$  is expressed in microvolts and  $t_{68}$  in degrees Celsius (1968). This relation was found to be valid over the range -197 to +1200 °C to within the estimated limits of experimental uncertainty (about  $\pm 1 \mu V$  below 600 °C, increasing to about  $\pm 2 \mu V$  at 1200 °C). There was insufficient data available to substantiate the validity of the relation outside this temperature range. However, data available from other high-purity platinum wires support its extrapolation to higher temperatures, but not to lower temperatures. At very low temperatures most high purity metal wires become unduly sensitive thermoelectrically to minute amounts of trace impurities. The quantitative results given above were obtained with specimens of Pt-67 wire which had been electrically annealed in air for 10 minutes at 1200 °C and slowly cooled to room temperature.

The various methods for characterizing thermocouples at high temperatures have been described in considerable detail by Roeser and Lonberger [13]. The two main high-temperature methods of characterization, thermoelectric voltage and temperature coefficient of resistance, have moderate sensitivity. A more sensitive measure of both the effective electrical purity and the state of physical perfection is the residual resistance ratio,

$$RRR = \frac{R(273 \text{ K})}{R(0 \text{ K})}$$

The residual resistance  $R(0 \text{ K})$  is well approximated for most metals by the resistance at liquid helium temperatures, about 4.2 K. For most metal specimens, there is no further decrease of resistance below 4.2 K. Bulk specimens may be characterized by the eddy current decay method which has been described in a previous OSRM publication by Clark et al. [14]. Thin wires may be characterized by the more simple four-probe electrical resistance method. Values of RRR were determined from liquid helium and ice point resistance measurements for five specimens taken at equally separated points along the lot of Pt-67 wire. The measured values are shown in figure 1. The average ratio for these five measurements is 3496. Specimen preparation prior to these tests consisted of cleaning in aqua regia for 12 minutes at 50 °C, rinsing in distilled water, annealing in air at 600 °C for 1 hour, and slow cooling to room temperature. It should be noted that this method is sufficiently precise to show inhomogeneity variations not clearly observed utilizing other methods.

The principal measurements made to characterize this wire as a cryogenic thermoelectric standard were performed in cryogenic comparators specifically designed to minimize handling and temperature cycling damage to the standard and test wires. A description of these comparators and their use is given in the next section.

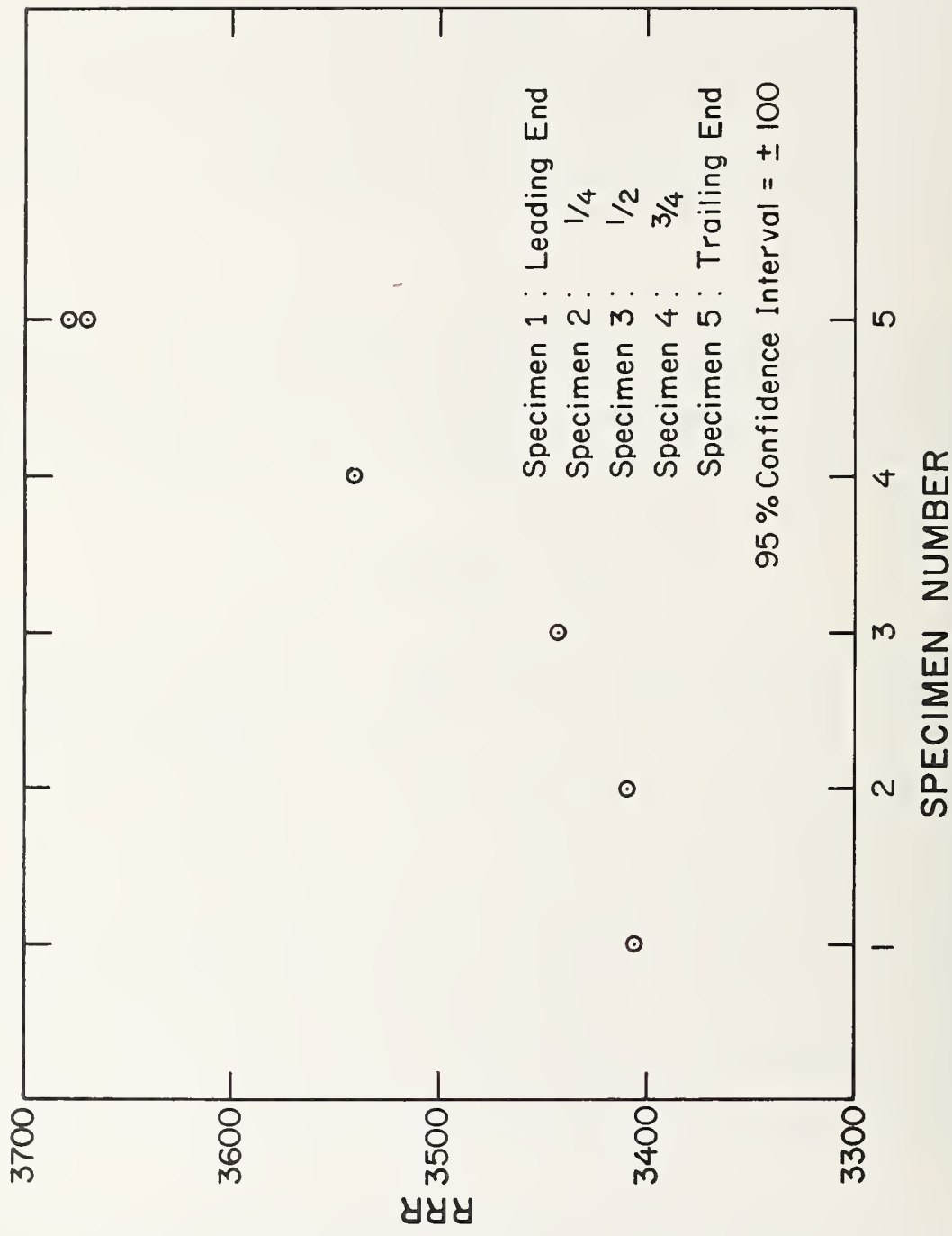


Fig. 1. Residual resistance ratio for five specimens from Pt-67.

The melting point of high-purity platinum is used as one of the secondary fixed points in the IPTS-68. Its assumed temperature is 1772 °C. However, Quinn and Chandler [15] of the National Physical Laboratory in Teddington, England, have more recently carried out extremely well controlled experiments on the melting point of platinum and have determined a value of  $1767.6 \pm 0.3$  °C. Their paper includes a detailed discussion of the effects of possible impurities and systematic experimental errors. Similar discrepancies and variations in realizing thermodynamic temperatures from determinations of the IPTS-68 temperatures can be significant for accurate thermophysical measurements. Those variations and the resultant precautions that are necessary are described more fully in section 5.

For accurate thermometry, one must insure that the temperature sensor truly measures the desired unknown temperature and is not affected significantly by the external environment. Some of the necessary experimental precautions have been described by Hust, et al. [16] for low temperatures and by Roeser and Lonberger [13] for high temperatures. Estimates of errors caused by poor thermal insulation or tempering can be calculated using standard heat transfer equations. An important physical parameter necessary for those heat transfer calculations is the thermal conductivity. Values of the thermal conductivity have been compiled by Childs, et al. [17] for low temperatures and by R. W. Powell, et al. [18] for high temperatures.

Values for other physical parameters of platinum are contained in standard handbooks and in two corporate publications by International Nickel Co. [19] and Engelhard Industries, Inc. [20].

#### 4. LOW-TEMPERATURE THERMOELECTRIC MEASUREMENTS

For any calibration experiment, whether it be at high or low temperatures, it is very important that the experimental method incorporate sufficient redundancy for meaningful statistical analyses. Unfortunately, this fundamental requirement is often overlooked. There are many ways in which statistically important comparisons may be incorporated into an experimental methodology. One of the simplest yet most powerful, was suggested by Youden [21] some years ago. The general method has been greatly expanded and made more rigorous utilizing the mathematical concepts of network or graph theory and the specific use of connectivity in those graphs [22,23]. Those developed methods have been incorporated into our publications on thermoelectric thermometry (e.g., 1,2). They were also used for the thermoelectric measurements reported in this Special Publication. Because of their importance to the reliable and accurate usage of this Standard Reference Material, an outline of their application to a simple four object measurement is described next.

As a simple illustration of how graph theory is applied, consider the situation where one is to intercompare some property of two different objects where two other intermediate objects are also available. Graphically this situation can be represented as in figure 2. In this figure, the objects are represented by the vertices and the comparison

of some property between objects is represented by the connecting lines. For example, the comparison  $a$  might represent the difference in weight between objects  $A$  and  $B$ . In applying graph theory to thermoelectric measurements, the vertices represent the thermocouple test wires and the connecting lines represent the thermal voltages generated by a given temperature gradient. The thermoelectric voltage between  $A$  and  $C$  in figure 2 would be determined by (1) measuring  $c$ , that is, a direct measurement of the desired voltage, (2) measuring the thermal voltages  $a$  and  $b$  and combining these data algebraically, and (3) measuring the thermal voltages  $d$  and  $e$  and similarly combining these data. The algebraic combination of  $a + b$  and  $d + e$  yield two additional independent determinations of the desired voltage equivalent to  $c$ . The final determination of the voltage ( $A-C$ ) is given by:

$$e_{calc} = (A-C) = [2c + (a+b) + (d+e)]/4. \quad (1)$$

The measurement  $c$  is given a weight of 2, since it involves only one experimental determination, whereas the other two measurement paths both require two readings. The estimate of the variance for ( $A-C$ ) is given by:

$$s^2 = \left\{ 2[e_{calc} - c]^2 + [e_{calc} - (a+b)]^2 + [e_{calc} - (e+d)]^2 \right\} / 3. \quad (2)$$

The advantages of taking data in this way are that it randomizes potentiometer dial or multimeter output errors, eliminates any subconscious operator prejudice, and randomizes spurious voltages in the lead wires. The magnitudes of  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  usually vary considerably; this means that the potentiometer dial or multimeter settings are also considerably different. Any setting errors which exist are randomized by this method. These random errors would then appear as scatter in the data and would be accounted for in the variance calculated from equation 2.

Since the potentiometer or multimeter readings vary a great deal and the order of readings may be random, the chance for subconscious operator prejudice is minimized. In order to influence the readings in a systematic way, the operator would have to algebraically combine very different numbers which are not necessarily taken in adjacent readings. This is not done subconsciously, even on the simple four object system being considered here. On the other hand, if multiple readings are taken of the same quantity, there is a strong tendency to produce data which are biased in a systematic way that falsely reduces the apparent imprecision.

Spurious voltages in the extension wires are also randomized by using the graph theory method: Consider a three wire system such as that which would result if the  $D$  wire were eliminated from figure 2. Assume the number we actually want is ( $B-C$ ). This is the thermoelectric voltage generated by the thermocouple made from materials  $B$  and  $C$  when a thermal gradient,  $\Delta T = T_1 - T_2$ , exists. The number which is actually measured is  $b$  which includes the spurious voltages generated in the

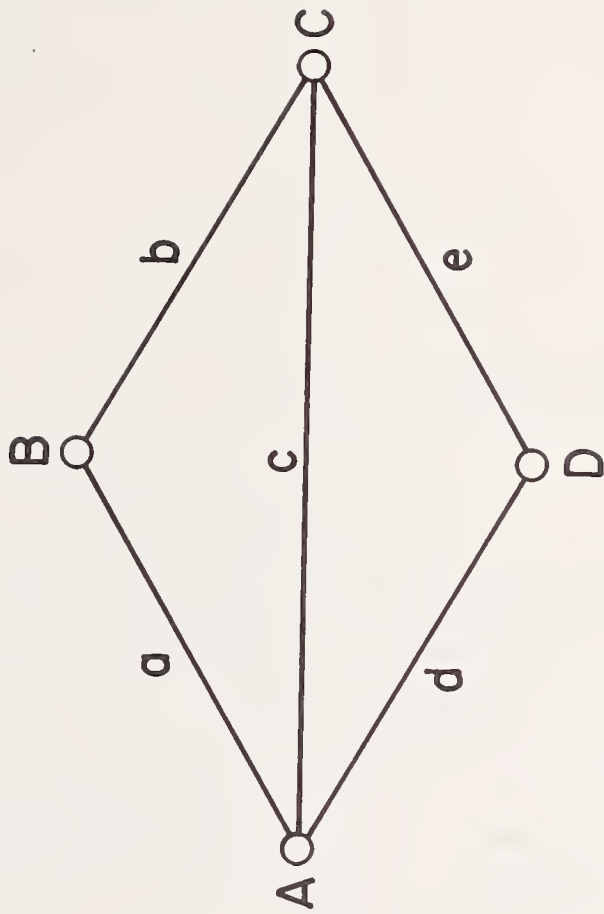


Fig. 2. Four object measurement graph.

extension wires to both  $B$  and  $C$ . If the spurious voltages  $\delta_{Bi}$  and  $\delta_{Ci}$  are zero or are at least known, then the true value of  $(B-C)$  may be determined. The voltages  $\delta_{Bi}$  and  $\delta_{Ci}$  can be determined by an isothermal test where  $T_1 = T_2$ . When  $T_1 = T_2$ ,  $(B-C) = 0$  and  $b = (B-C) + \delta_{Bi} + \delta_{Ci} = \delta_{Bi} + \delta_{Ci}$ .

However, this determination of the spurious voltages is valid only when the thermal gradients in the system are the same as when the isothermal test was made. In many experimental situations this approach to the spurious voltage problem is not practical. The only other solution is to randomize these voltages so that they appear as scatter in the experimental data and are therefore included in the estimate of the variance,  $s^2$ . The graph theory approach does allow these voltages to be randomized. Suppose, for instance, that we wish to determine  $(B-C)$  in figure 2. The voltages  $a$ ,  $b$ , and  $c$  would then be measured.

$$a = (B-A) + \delta_{A1} + \delta_{B1}$$

$$b = (B-C) + \delta_{B2} + \delta_{C1}$$

$$c = (A-C) + \delta_{A2} + \delta_{C2}$$

$$b_{\text{calc}} = [b + \frac{1}{2}(a+c)]/3/2 = \frac{2b+a+c}{3}$$

$$b_{\text{calc}} = \frac{[2(B-C) + (B-A) + (A-C)]}{3} + \frac{\delta_{A1} + \delta_{A2} + \delta_{B1} + 2\delta_{B2} + 2\delta_{C1} + \delta_{C2}}{3}$$

If the spurious conditions are stable, i.e., the measurements are made rapidly enough that the system gradients haven't changed,

$$\text{then } \delta_A = \delta_{A1} = \delta_{A2}, \delta_B = \delta_{B1} = \delta_{B2}, \text{ and } \delta_C = \delta_{C1} = \delta_{C2}$$

$$\text{and } b_{\text{calc}} = \frac{[2(B-C) + (B-A) + (A-C)]}{3} + \frac{2}{3}\delta_A + \delta_B + \delta_C.$$

If the more common procedure of multiple readings of  $b$  were used,  $b$  would be measured, say, 3 times:

$$b_1 = (B-C)_1 + \delta_B + \delta_C,$$

$$b_2 = (B-C)_2 + \delta_{B1} + \delta_{C1},$$

$$b_3 = (B-C)_3 + \delta_{B2} + \delta_{C2}, \text{ and}$$

$$b_{\text{calc}} = \frac{[(B-C)_1 + (B-C)_2 + (B-C)_3]}{3} + \frac{\delta_B + \delta_C + \delta_{B1} + \delta_{C1} + \delta_{B2} + \delta_{C2}}{3}.$$

Again, assume stable spurious conditions for the time required to determine  $b$  three times. Then  $\delta_B = \delta_{B1} = \delta_{B2}$ ,  $\delta_C = \delta_{C1} = \delta_{C2}$ , and  $b_{\text{calc}} = (\overline{B-C})_{1,2,3} + \delta_B + \delta_C$ .



The tendency to randomize dial errors and to eliminate operator prejudice is illustrated by comparing  $b_{calc}$  from the graph theory method and from the multiple readings method. More dials or output readings are probably changed in determining  $(B-C)$ ,  $(B-A)$ , and  $(A-C)$  than are changed in determining  $(B-C)$  three times. The subconscious operator prejudice is reduced by having to combine the two readings  $(B-A)$  and  $(A-C)$  to get the independent determination of  $(B-C)$ .

The third and perhaps the most important advantage of the graph theory approach to the measurement of thermocouple outputs is the randomization of spurious voltages in the extension wires. These errors would not be accounted for, i.e., they would introduce a systematic bias, if the multiple reading approach is utilized. This is shown in the calculation of the estimate of variance for the two methods:

First by graph theory:

$$b_{calc} = \frac{[2(B-C) + (B-A) + (A-C)]}{3} + \frac{\delta_{A1} + \delta_{A2} + \delta_{B1} + 2\delta_{B2} + 2\delta_{C1} + \delta_{C2}}{3}$$

$$S^2_{b_{calc}} = \{2(b_{calc} - b)^2 + [b_{calc} - (a+c)]^2\} / 2;$$

now assume that the only cause of variation is the spurious voltages:

$$S^2_{b_{calc}} = 1/3(\delta_{A'} + \delta_{B'} - \delta_{C'})^2$$

$$\text{where } \delta_{A'} \equiv \delta_{A1} + \delta_{A2},$$

$$\delta_{B'} \equiv \delta_{B1} - \delta_{B2}, \text{ and}$$

$$\delta_{C'} \equiv \delta_{C1} - \delta_{C2}.$$

If spurious conditions are constant,  $\delta_{B'} = 0$ ,  $\delta_{C'} = 0$  and  $S^2_{b_{calc}} = 1/3\delta_{A'}^2$ .

Second, by multiple measurements:

$$b_{calc} = \frac{[(B-C)_1 + (B-C)_2 + (B-C)_3]}{3} + \frac{\delta_B + \delta_C + \delta_{B1} + \delta_{C1} + \delta_{B2} + \delta_{C2}}{3};$$

$$S^2_{b_{calc}} = \{(b_{calc} - b_1)^2 + (b_{calc} - b_2)^2 + (b_{calc} - b_3)^2\} / 2$$

again assuming all scatter is due to spurious voltages, e.g.,

$$(B-C)_1 = (B-C)_2 = (B-C)_3, \text{ then}$$

$$18 S^2_{b_{calc}} = [-2(\delta_B + \delta_C) + \delta_{B1} + \delta_{C1} + \delta_{B2} + \delta_{C2}]^2$$

$$+ [-2(\delta_{B1} + \delta_{C1}) + \delta_B + \delta_C + \delta_{B2} + \delta_{C2}]^2$$

$$+ [-2(\delta_{B2} + \delta_{C2} + \delta_B + \delta_C + \delta_{B1} + \delta_{C1})]^2.$$

Now if the spurious conditions are constant

$$\delta_B = \delta_{B1} = \delta_{B2}, \delta_c = \delta_{c1} = \delta_{c2}, \text{ and } S_{b\text{calc}}^2 = 0.$$

The spurious voltages do not appear in the estimate of the standard deviation when the multiple measurement method is used. They are truly present but unaccounted for until some estimate of systematic error is introduced.

In other words, the calculated standard deviation using graph theoretical methods is usually larger than that obtained using simply repeated measurements. However, it is much more representative of the true experimental uncertainty. Likewise, calculated values for quantities such as the voltages a, b, or c are more representative of their true mean values. The method also has the twin advantages of spot-lighting erroneous readings when they do occur and allowing substitution values to be inserted into the data sets when some value is obviously in error or is lost.

#### 4.1. Thermocouple comparator

The thermocouple comparator to be discussed here is basically a mechanical support which allows thermoelectric intercomparison between standard reference wires and a test wire without damaging the reference wires. Figures 3a and 3b show the essential details of the design used here; complete details are given in a preceding publication in this series [10]. The two tubes containing the test and standard specimens are dipped into reference baths, e.g., liquid helium, liquid nitrogen, ice slush mixture, etc. For the thermoelectric results presented below, Table 4, the two legs were inserted into liquid nitrogen boiling at atmospheric pressure and an ice slush and water mixture at 0 °C. Figure 4a is an electrical schematic of a two wire differential thermocouple. Figure 4b extends the same configuration to a four wire system such as the one we use in our thermoelectric comparators. All thermoelectric combinations are accounted for in the six measurements indicated in this figure. Using graph theory [1] and thermoelectric additivity principles [24,25], one can get four independent determinations of any thermocouple pair; e.g., if  $E_{T1}$  is needed, each of the following equations represent a nonredundant, independent determination of  $E_{T1}$ :

$$(6) \quad E_{T1} = E_{T1}$$

$$(3) \quad E_{T1} = E_{T2} - E_{12}$$

$$(3) \quad E_{T1} = E_{T3} - E_{13}$$

$$(2) \quad E_{T1} = E_{T3} - E_{12} - E_{23}.$$

The relative weighting, assuming the same variance for each measured voltage, is shown in parenthesis before each equation. The average value of  $E_{T1}$  is given by:

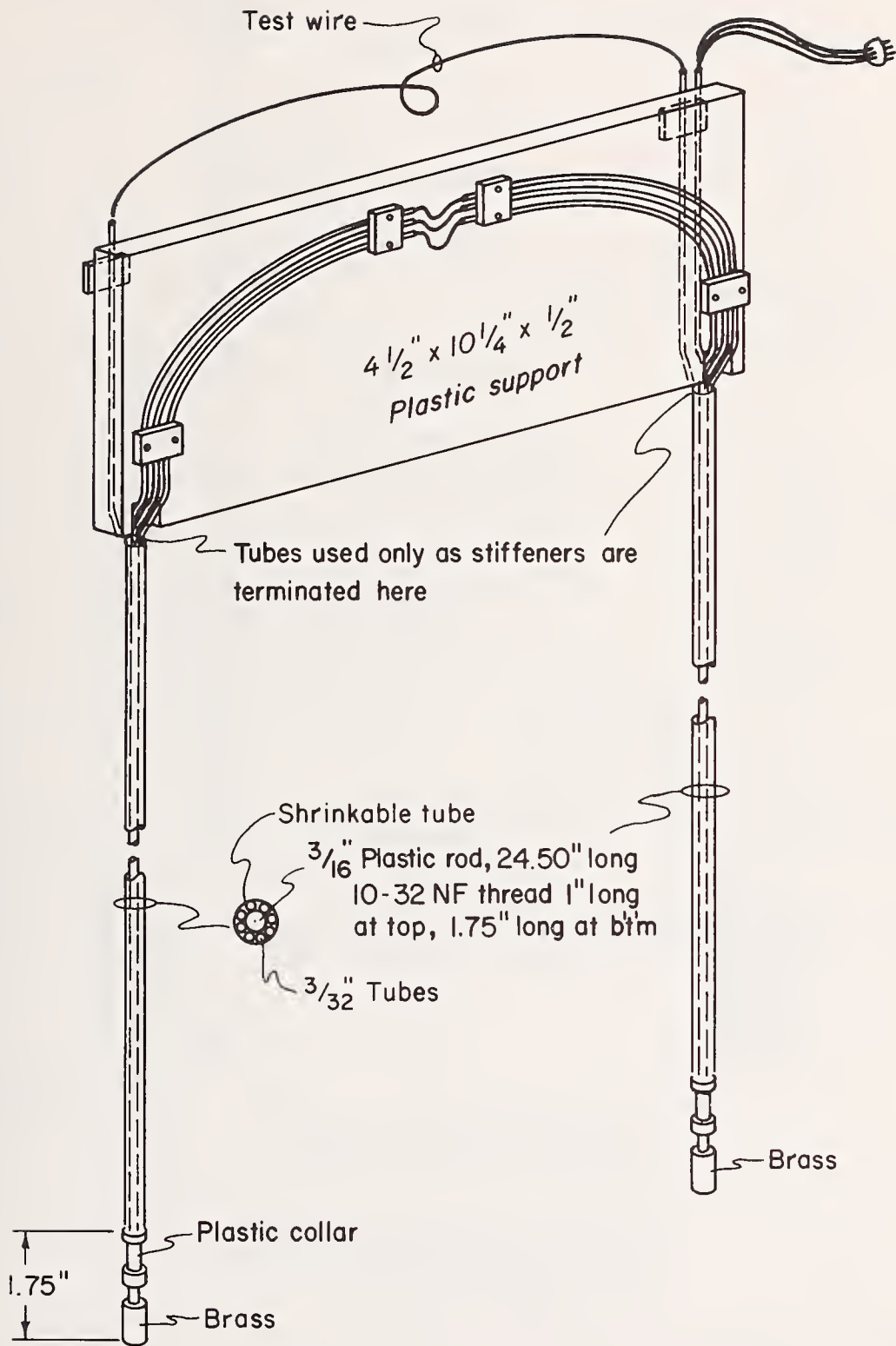


Fig. 3a. Details of thermocouple comparator (pictorial view).

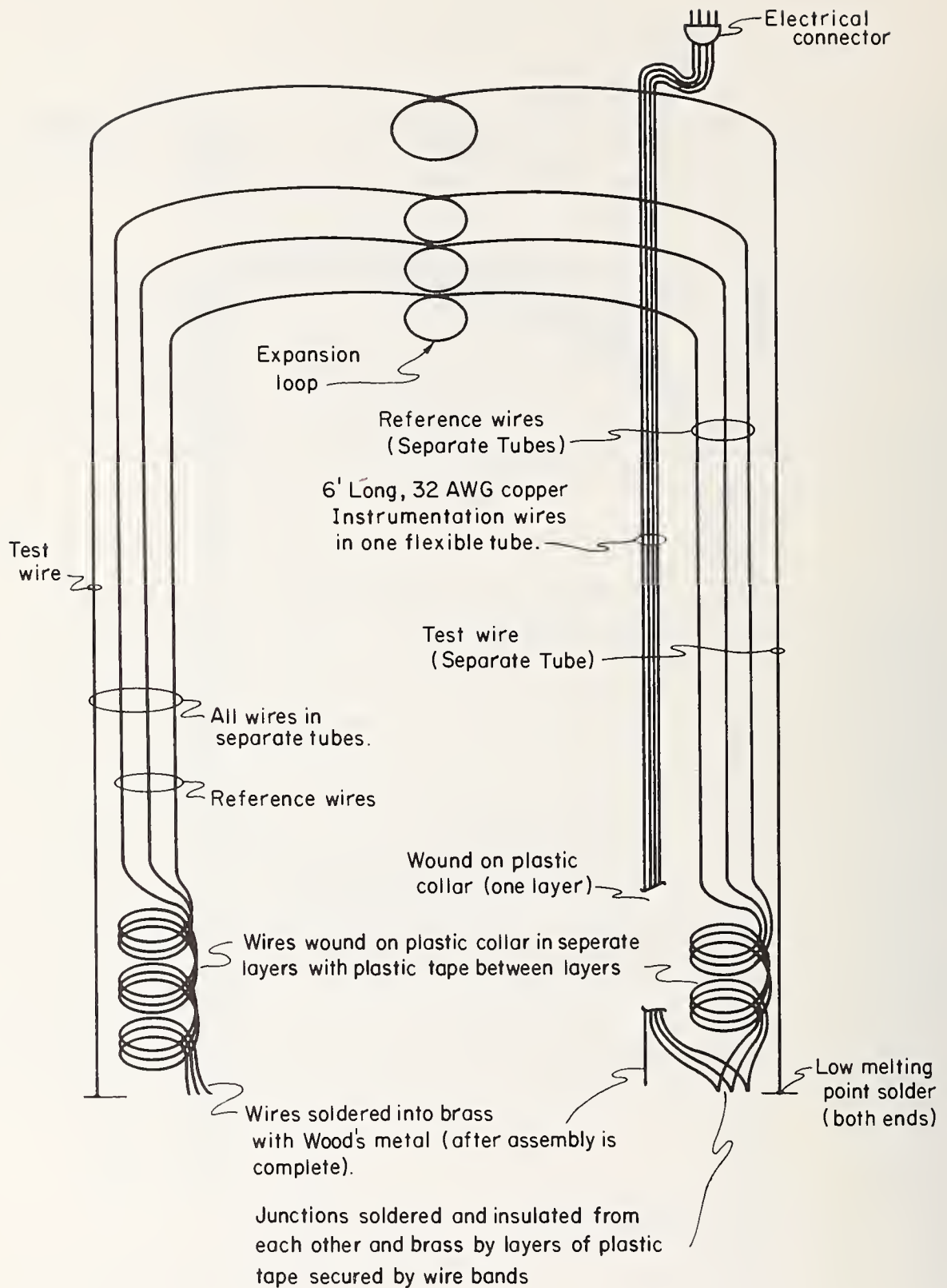


Fig. 3b. Details of thermocouple comparator (wiring diagram).

Table 4. Thermoelectric Voltage of Pt-67 versus commonly used thermocouple wire between liquid nitrogen (76 K) and the ice (273.15 K) fixed point.

<u>Thermocouple</u>	<u>EMF, <math>\mu</math> V*†</u>	<u>Sensitivity at 76K (<math>\mu</math>V/K)</u>
KP or EP** vs Pt-67	3401.0 $\pm$ 0.5	5.4
TP** vs Pt-67	207.6 $\pm$ 0.5	4.3
Pt-67 vs TN**	5350.0 $\pm$ 0.5	20.4
Pt-67 vs KN**	2445.1 $\pm$ 0.5	10.4
Pt-67 vs SRM 733††	221.9 $\pm$ 0.5	6.2

\* The data for Pt-67 versus KP, KN, TP, and TN were computed from earlier data by Sparks et al. [1] and more recent comparisons of the thermoelectric voltage of Pt-67 and the platinum wire used in [1]. The value for Pt-67 versus SRM 733 was obtained by direct comparison in the Pt-67 comparator discussed in this paper.

† The uncertainties given are twice the estimated standard deviations.

\*\* EN or TN A copper-nickel alloy, constantan, Cupron [40], Advance [41], Thermo Kanthal JN [42].  
 KP or EP A nickel-chromium alloy, Chromel [43], Tophel [40], T-1 [41], Thermo Kanthal [42].  
 KN A nickel-aluminum alloy, Alumel [43], Nial [40], T-2 [41], Thermo Kanthal [42].  
 TP Copper, usually electrolytic tough pitch.

The use of trade names does not constitute an endorsement of any manufacturer's products. Any materials manufactured in compliance with established standards are equally suitable.

†† SRM 733 is a Ag-28 at % Au alloy. This SRM is described in detail in [10].

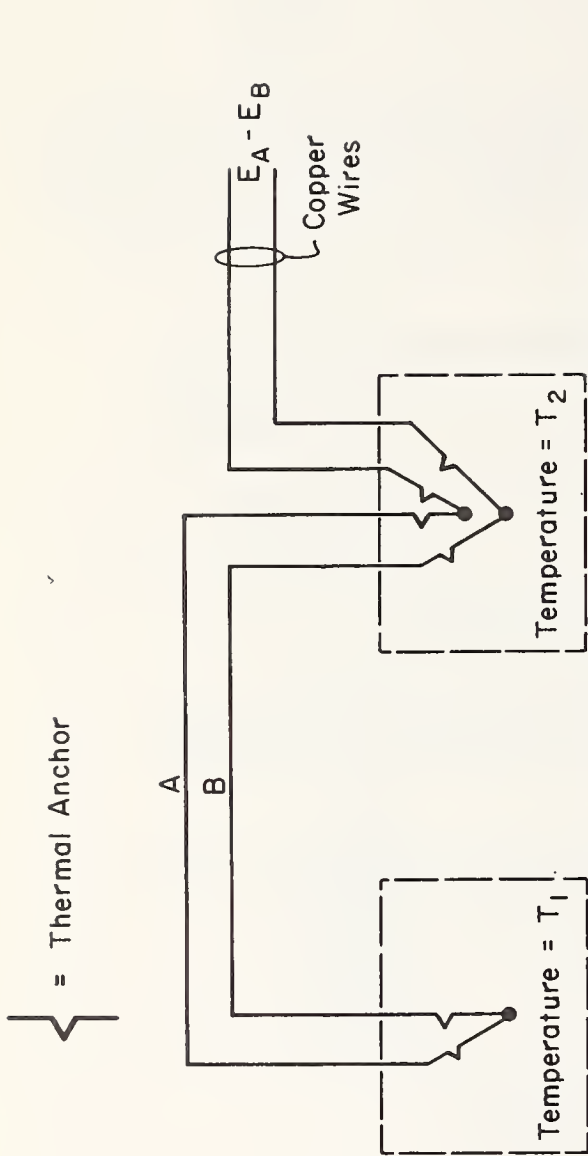


Fig. 4a - TYPICAL THERMOCOUPLE ARRANGEMENT

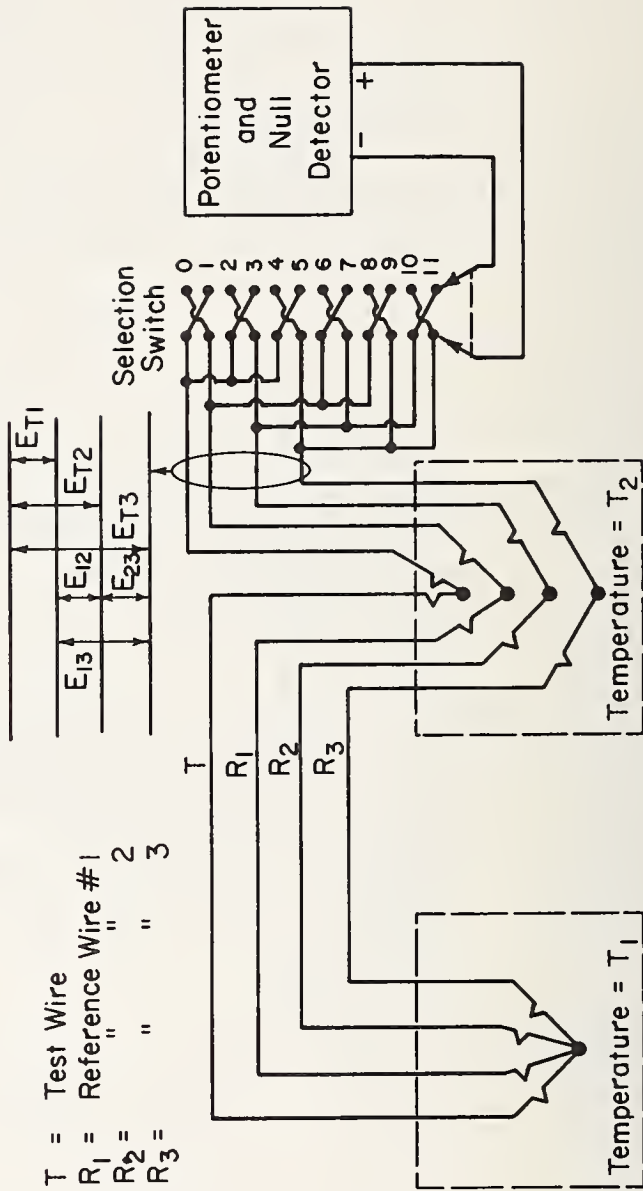


Fig. 4 b - COMPARATOR CIRCUIT for CALIBRATION of STANDARD REFERENCE THERMOCOUPLE WIRES

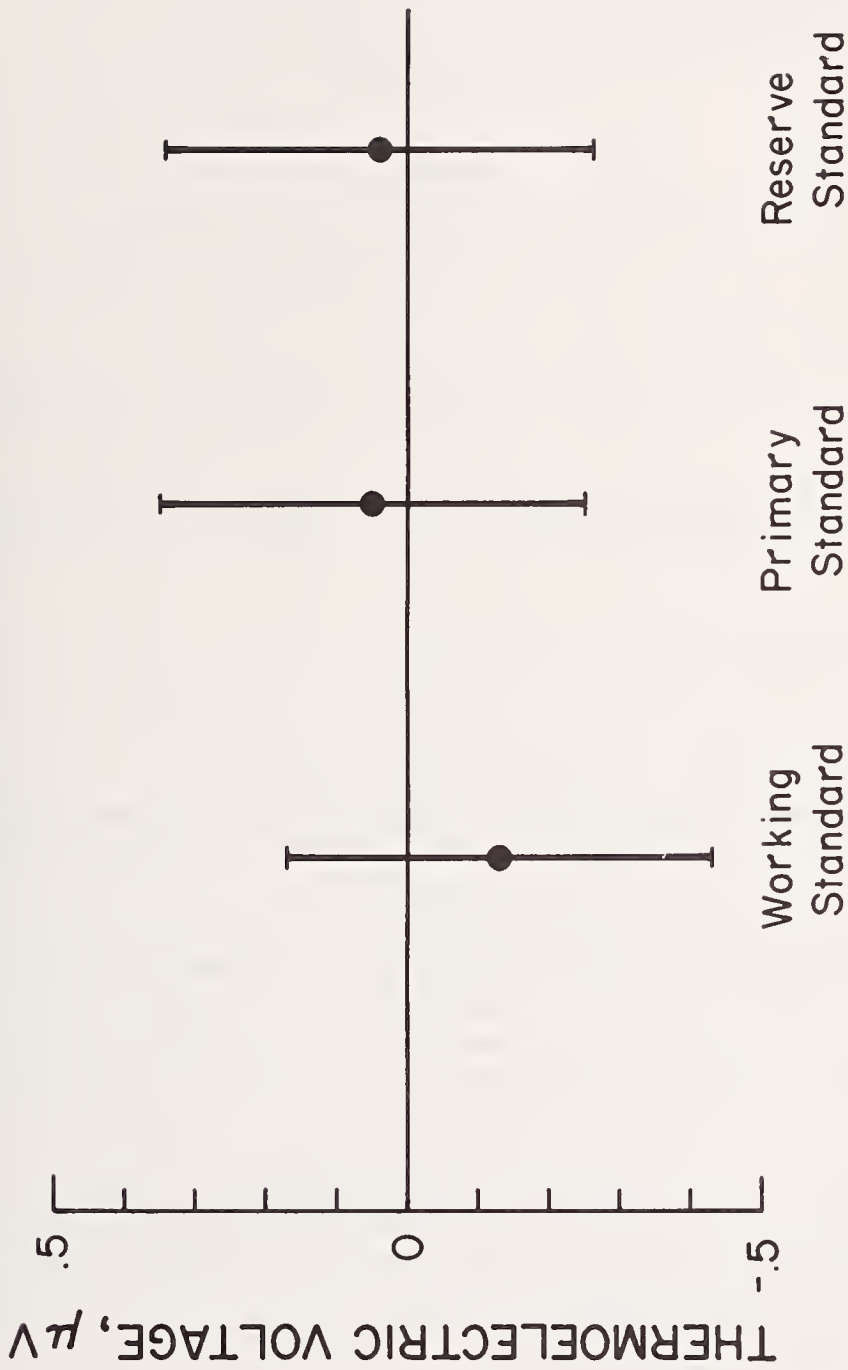


Fig. 5. Intercomparisons of three Pt-67 comparators between 76 and 273.15 K via a common thermocouple wire. The error bars are  $\pm 2\sigma$  values.

$$\bar{E}_{T1} = [6E_{T1} + 3(E_{T2} - E_{12}) + 3(E_{T3} - E_{13}) + 2(E_{T3} - E_{12} - E_{23})]/14.$$

It is suggested that similar data be taken with different immersion depths so that different sections of the wires are exposed to the temperature gradient at the liquid-gas interface. Also, repeat data should be taken with the legs of the comparator reversed in the fixed point baths. These redundant data are necessary to obtain a value for the degree of scatter (variance) caused by spurious signals.

The determination of the thermoelectric voltage of a test wire with respect to the standard reference thermocouple wire is summarized below:

- (1) Record the six voltages illustrated in figure 4b.
- (2) Repeat step 1 for three immersion depths to randomize spurious voltages.
- (3) Repeat (1) and (2) with comparator reversed in the baths.
- (4) Compute the most probable values of the six sets of six voltages using all of the redundancy in the data, both for the forward and reverse directions.
- (5) Compute the average voltage for the test wire with respect to the reference standard:

$$\bar{E}_{TR} = (E_{T1} + E_{T2} + E_{T3})_F / 3 + (E_{T1} + E_{T2} + E_{T3})_R / 3] / 2.$$

Also calculate the variance of this voltage. This variance is based upon the random scatter indicated by the redundancy of these measurements.

The values  $E_{12}$ ,  $E_{13}$ , and  $E_{23}$ , similarly determined, are used to detect possible systematic changes among the reference wires. Control charts of  $E_{12}$ ,  $E_{13}$ , and  $E_{23}$  will be maintained to detect such changes in the comparators. To further reduce the possibility of undetected changes in reference wires, three comparators have been built. The first or working standard will be used for routine testing; the second or primary standard will be used occasionally for comparison to the working comparator. The third comparator will be considered as a replacement for either of the others. Occasional intercomparisons will be made among all three comparators. Figure 5 illustrates the present intercomparisons of these three comparators between 76 and 273 K. These measurements were made on a common transfer wire; the transfer wire was annealed at 1100 °C before each measurement.

The procedure used to prepare the Pt-67 wires for test in the thermoelectric comparators is as follows: degrease the wire in freon, rinse in distilled water, and then anneal. The effect of annealing temperature was investigated by performing thermoelectric comparisons on wires annealed at 400 °C, 1100 °C, and 1200 °C. The anneals at 1100 °C and 1200 °C are obtained by passing on electrical current through the



specimens and thereby resistance heating them. A thermoelectric difference of  $0.41 \mu\text{V}$  was observed between the wires annealed at  $400$  and  $1100$  °C. No difference was observed between the  $1100$  and  $1200$  °C anneals. The  $1100$  °C anneal, adopted for use to prepare this thermoelectric standard, is as follows: resistance heat in air to  $1100$  °C, hold for four minutes, cool to room temperature in about 2.5 minutes. Slow cooling of the wire is necessary in order to minimize quenching in vacancies. This annealing procedure produces wires which are indistinguishable from each other and are apparently strain free since they are thermoelectrically the same as wires annealed at  $1200$  °C for a significantly longer time.

The five wires which were chosen to represent the entire lot of Pt-67 and were previously characterized by RRR measurements (see figure 1) were compared to the standard reference wires in the working comparator between  $76$  and  $273$  K. These results, illustrated in figure 6, show that no systematic variation in thermoelectric voltage is detectable along the entire length of Pt-67. Variation of the Seebeck coefficient ( $dE/dT$ ) caused by material variability is thus within the measurement error of the system, approximately  $0.002 \mu\text{V/K}$ .

The cryogenic comparators were designed and will be maintained in the Cryogenics Division by one of the authors (L.L.S.).

## 5. HIGH-TEMPERATURE THERMOELECTRIC MEASUREMENTS

The high-temperature comparator is very similar in concept to the low-temperature one described in the previous section. The schematic drawing, figure 7, shows the apparatus designed and used by members of the Temperature Section, Heat Division of the National Bureau of Standards in Gaithersburg, Maryland. The main conceptual differences in the techniques are that the high-temperature method uses repeated measurements rather than graph networks for statistical redundancy and the high temperature furnace has variable temperatures which must be determined by reference thermocouple thermometers. The more apparent differences are that the high temperature specimens are held horizontally rather than vertically and the electrical switching circuit is different because of the different type of data redundancy.

The high temperature methodology is also, quite naturally, very similar to that used at low temperatures. The platinum test wires are washed with ethanol and are not etched with any cleaning acid. They are then annealed at  $1200$  °C in air for 10 minutes, cooled over a 1 minute period to  $750$  °C where they are held for 30 minutes. If the material is part of a Type S or R thermocouple, it is annealed first at  $1450$  °C for 45 minutes and then cooled to  $750$  °C and held there for 30 minutes. In both circumstances the wire is heated electrically by an ac current that flows through the wires from temporary clamps attached near the ends of the wires. The annealing is performed in a cabinet to reduce the effects of variable air currents and possible dust contamination.

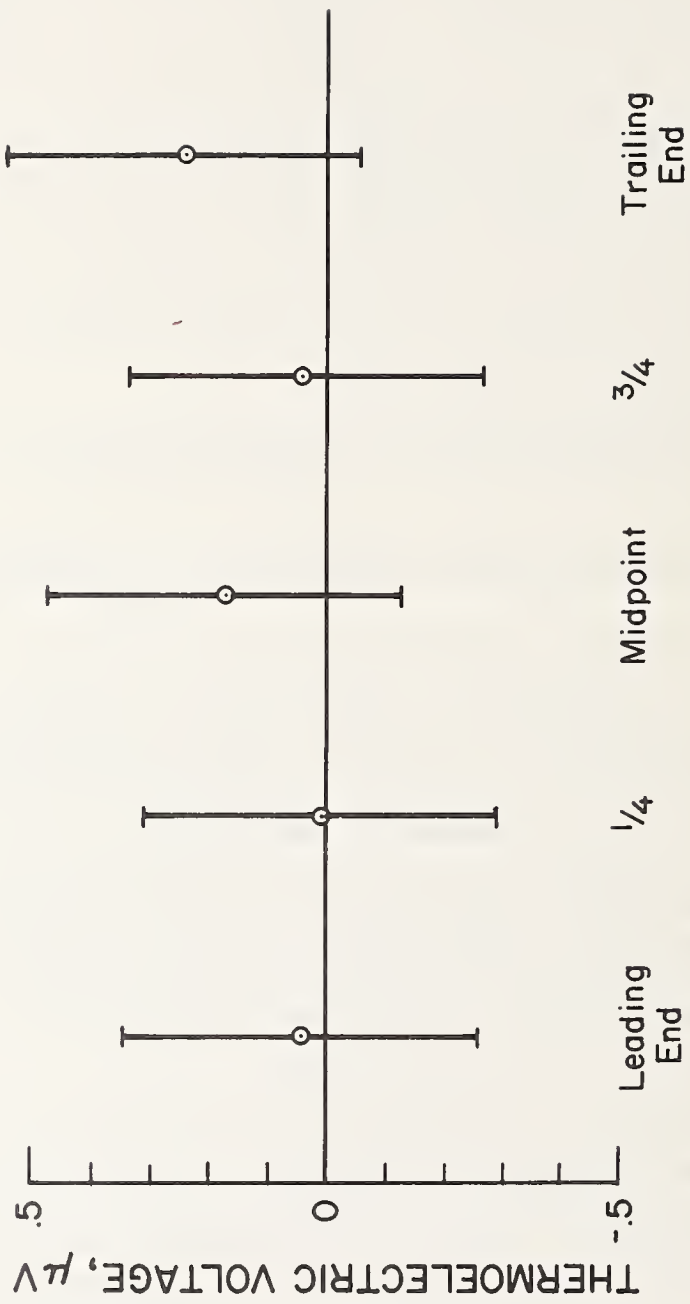


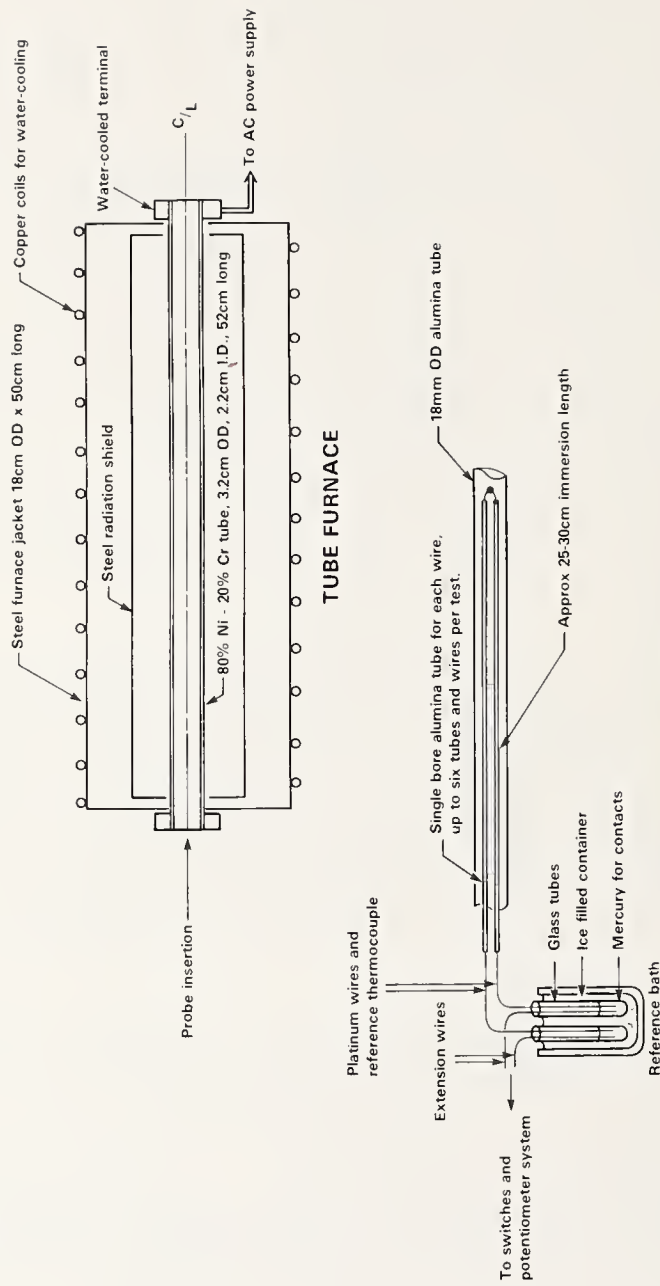
Fig. 6. Thermoelectric comparisons of Pt-67 between 76 and 273.15 K at equally spaced points along the entire length in stock.

The annealed wires, usually about one meter long, but at least 60 cm, are threaded through single bore high purity alumina tubes that are about 40 to 50 cm long. Care must be exercised during threading to minimize the effects of work hardening. At least one Type S positive thermoelement (Pt-10% Rh) is also assembled with each test batch of platinum thermoelements so that the test temperature can be determined. Up to six tubes and wires (including any Type S or Type R positive material being calibrated at the same time) are then inserted into a larger (18 mm o.d.) alumina tube for further protection. All of the test wires and the temperature reference thermoelement are welded together at the end that will be immersed in the furnace. In order to reduce the effects of variable temperature gradients and cooling of the test junction, the wires are always immersed at least 25 to 30 cm into the furnace and the welded junction is placed near the center of the furnace. Because of the welded junction, about 2 to 6 mm of the reference platinum material is consumed for each calibration run. The end of each wire opposite to the welded junction is immersed in a reference bath and joined to a wire that goes to the switch and potentiometer system. The reference bath is a carefully prepared ice-water mixture contained in an insulated glass vessel. Each test wire and its connecting lead wire are inserted in a separate small glass tube that contains some mercury in the bottom for electrical contact. Each tube with its wires is inserted into the ice bath reference and a cover is placed over the reference bath to minimize the effects of radiation and air convection.

Calibration tests are run at many different temperatures, but the most common are near the freezing points of antimony, silver, and gold (630.74, 961.93, and 1064.43 °C respectively). It usually takes about one-half hour for a suitable thermal equilibrium to be obtained by the furnace and thermoelement system. The test temperature is determined by the incorporated calibrated Type S thermocouple as measured by a potentiometer system. When the calibrated thermometer indicates the proper temperature, the voltage of the test thermoelements is measured by another potentiometer system.

As indicated above, a small amount of the reference platinum thermoelement is consumed for each calibration run. In order to prevent the complete depletion of the primary Pt-67 (SRM 1967) material, secondary reference wires are used for the routine calibrations. The secondary materials calibrated against the primary lot. In this manner the primary material should be maintained for many years, yet all calibrations are traceable to the primary Pt-67 material. The primary reference material is maintained by G. W. Burns of the Temperature Section in NBS, Gaithersburg.

The International Practical Temperature Scale of 1968, labeled IPTS-68, uses a platinum-10% rhodium versus platinum thermocouple (Type S) as the interpolating standard for the temperature range from the antimony freezing point, 630.74 °C, to the gold freezing point, 1064.43 °C, with the silver freezing point, 961.93 °C, serving as an intermediate defining fixed point [6]. Discussions of the development of that scale were given by Preston-Thomas [26] and Bedford [27] at the Fifth Symposium on Temperature in 1971. Graphs of the thermoelectric voltage, Seebeck coefficient and its temperature derivative for the Type S thermocouple



TEST PROBE ASSEMBLY

Fig. 7. High temperature calibration system for platinum thermoelements.

are shown in figures 8, 9, and 10 (from reference 2). The circles indicate fixed point values, not experimental measurements. It is seen in Fig. 10 that the Seebeck derivatives in the temperature range from 630.74 to 1064.43 °C do not fit smoothly with those in the ranges above and below. Those deviations are caused by the arbitrary assignment in IPTS-68 of quadratic behavior to the thermoelectric voltage of Type S thermocouples.

It could well be expected that those discontinuities in slope at 630.74 and 1064.43 °C and the imposed quadratic behavior within the same temperature range would lead to observed differences between IPTS-68 and other thermodynamic or interpolating scales. Such a phenomenon has been observed and is becoming well documented. Quinn, et al. [28] and Bonhoure [29] have compared the thermoelectrically maintained IPTS-68 to radiation photoelectric pyrometer measurements. These authors clearly observe significant differences, becoming as large as 0.5 °C near 800 °C. To a lesser extent, the radiation measurements of Bonhoure [29,30] also question the thermodynamic temperature assigned to the silver and gold freezing points.

At the lower temperature reference point, 630.74 °C, the platinum thermoelectric scale joins the scale where interpolated temperatures are obtained by platinum resistance thermometers. The use of such thermometers has been exhaustively described in the recent Monograph by John Riddle and his colleagues of the Temperature Section [31]. Evans and Woods [32] have extended platinum resistance measurements from the antimony freezing point up to the gold point, 1064.43 °C. They also, as could be expected, find significant differences between the IPTS-68 temperatures and those derived by assuming a smooth variation of the electrical resistance of platinum. Their observed deviations, up to about 0.5 °C, agree qualitatively, and even semi-quantitatively, with those reported later by Quinn, et al. [28] and Bonhoure [29] using the completely different radiation technique.

The differences between temperatures based on the IPTS-68 platinum thermoelectric scale and the true thermodynamic scale can become important for highly accurate thermometric or thermodynamic measurements. These considerations will, however, not affect the use of platinum as a reference thermoelement for other thermocouple materials besides Types S and R platinum-rhodium alloys. Articles by Jones [33] and by McLaren and Murdock [34] describe in great detail the precautions one must make to obtain highly accurate thermoelectric measurements with platinum materials at high temperatures.

## 6. EFFECTS OF IMPERFECTIONS

The thermoelectric voltage of platinum, like most other electronic properties of pure metals, is more sensitive to impurities at low temperatures than it is at high temperatures. For that reason, pure platinum is not suitable as a thermoelectric Standard Reference Material below about 50 K. Therefore, SRM 1967 is not recommended for calibrations below the liquid nitrogen normal boiling point, 77.348K or -195.802 °C. In its

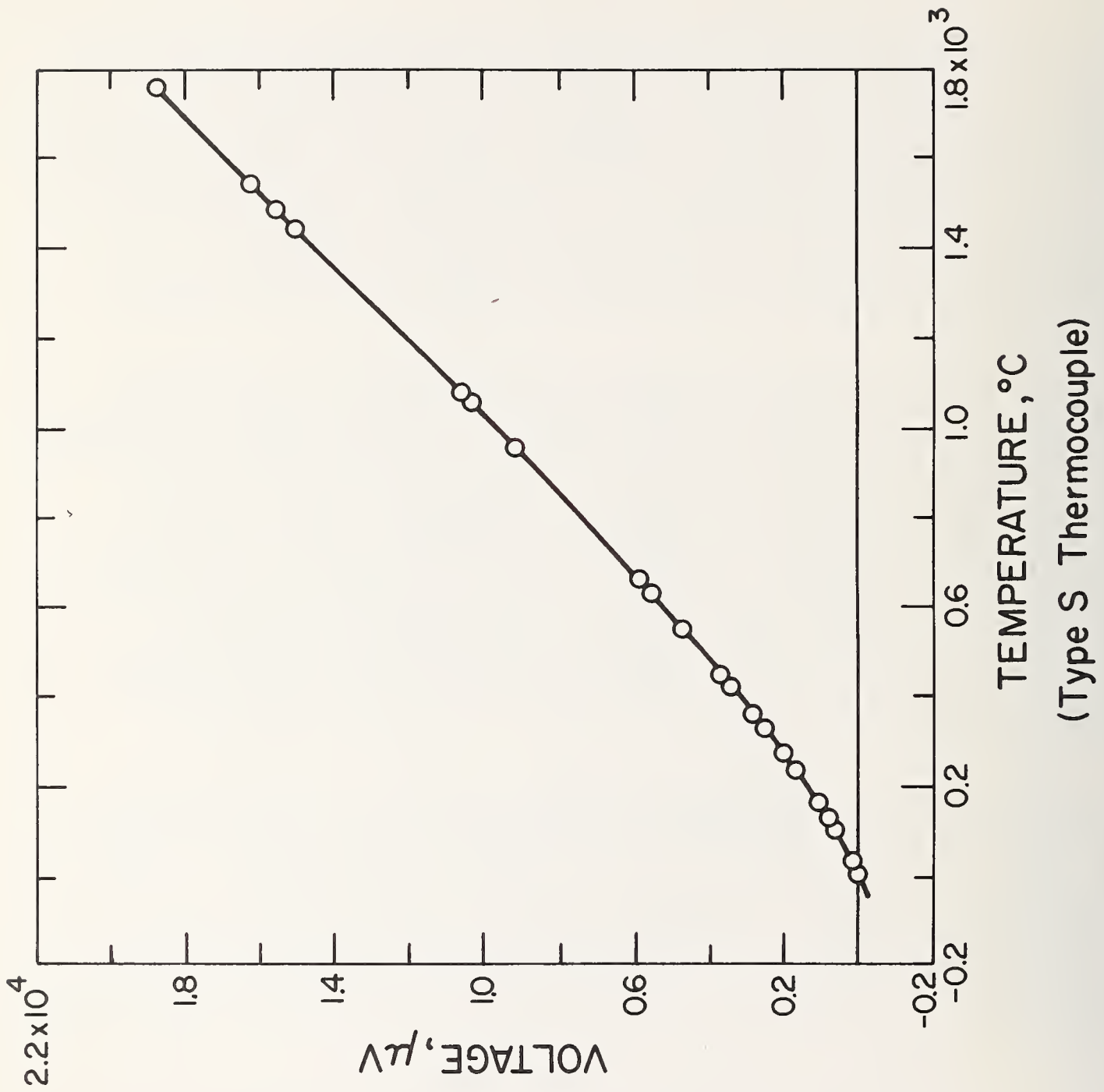
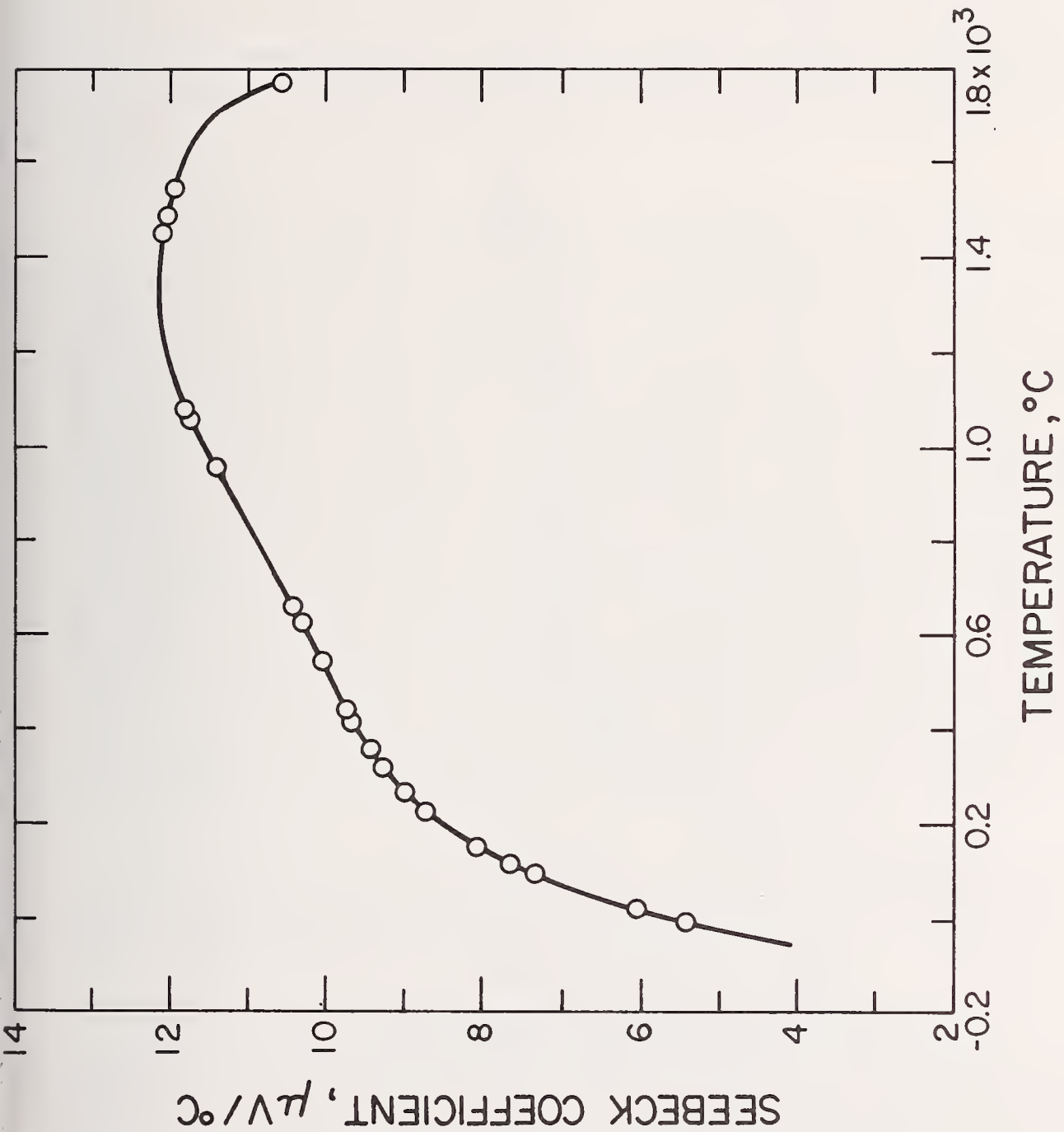
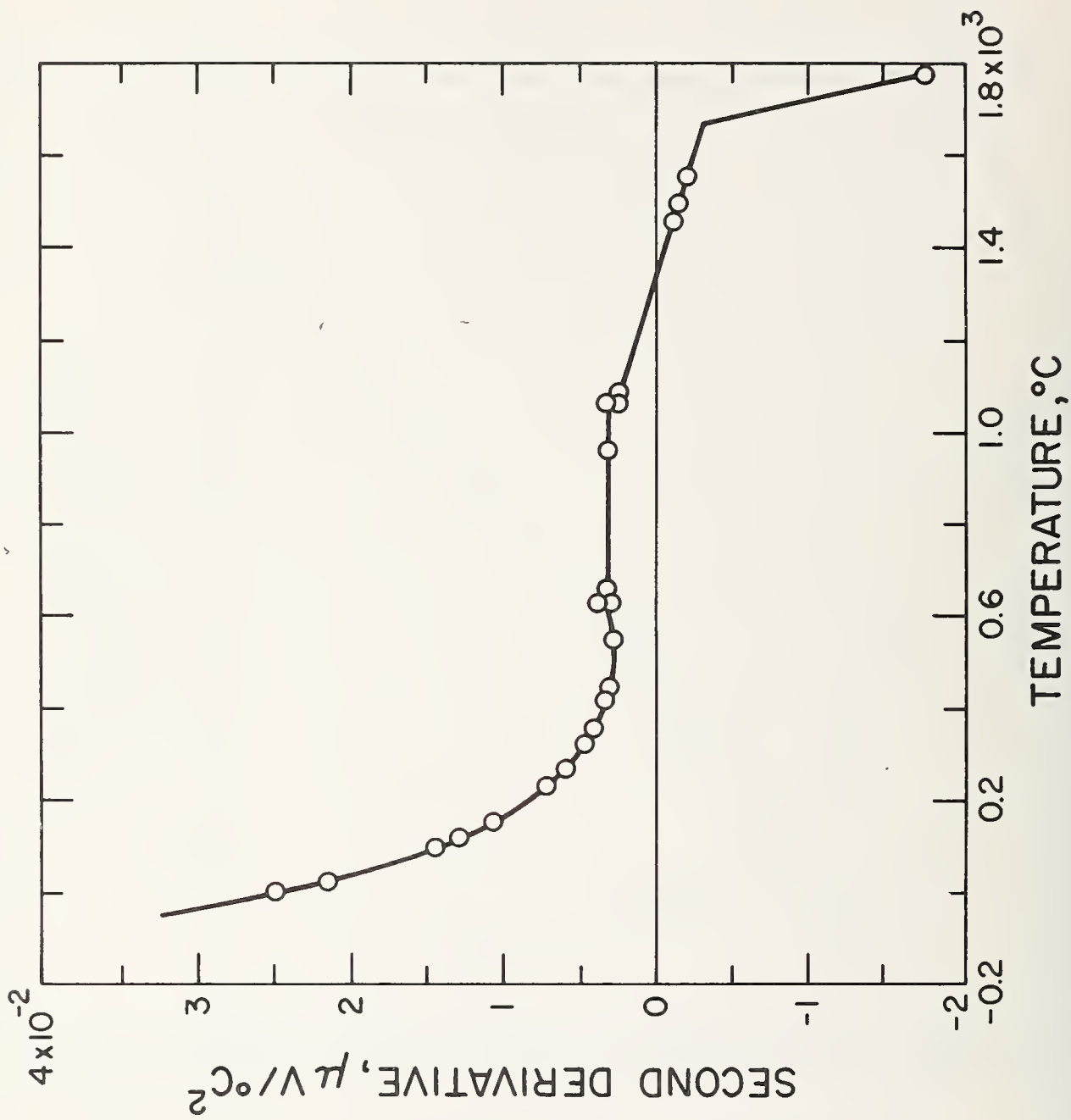


Fig. 8. Thermoelectric voltage for Type S thermocouples. The circles indicate values at various thermoelectric reference temperatures on the IPTS-68.



(Type S Thermocouple)

Fig. 9. Seebeck coefficient for Type S thermocouples. The circles indicate values at various thermoelectric reference temperatures on the IPTS-68.



(Type S Thermocouple)

Fig. 10. Second derivative of thermoelectric voltage for Type S thermocouples. The circles indicate values at various thermoelectric reference temperatures on the IPTS-68.



place the Ag-Au alloy, SRM 733, is recommended for use down to the liquid helium normal boiling point, 4.2K. Deviations of the voltages of three standard Pt-67 specimens are shown in figure 5 and of five specimens in figure 6. It is seen that the deviations range from 0.1 to 0.5  $\mu\text{V}$  for extremely carefully handled specimens with junctions at the ice point and at the liquid nitrogen normal boiling point. More recent results on two platinum Pt-67 wires mounted in a cryostat have been obtained by Burley, et al. [35] in their study on Nicrosil and Nisil alloys. The deviations shown in figure 11 indicate the amount of variation that can be observed in practical cryostats, even when great care is used in handling well-annealed specimens. The errors are larger near 0 °C because the reference bath was near 76 K and therefore there were larger thermal gradients for the higher temperature runs.

Vines [36], Rhys and Taimisulu [37], Cochrane [38] and Aliotta [39] have studied the effects of dilute or trace impurities on the high-temperature electrical properties of pure platinum. Cochrane's paper is thorough and up-to-date, especially in its discussion on Pt-67. He concluded, among many things, that the principal cause of thermoelectric inhomogeneities was radial chemical inhomogeneity caused by surface contamination, especially of iron, during the production process. The thermoelectric effectiveness of some impurities was found to depend on the melting and annealing of test specimens. The effect of an individual impurity was essentially linear and the total effect of all impurities was simply additive from the effects of each specific impurity. All impurities show a positive effect on the thermoelectric voltage except gold, which shows a slight negative effect. The largest specific effects for significant impurities (in  $\mu\text{V}/\text{ppm}$  weight) are shown by chromium, lead, silicon (if electrically active) and ruthenium. Because the iron concentration is usually much greater than that for any other impurity, the impurity effect on thermoelectric voltage is controlled primarily by the iron content. Cochrane [36] also includes much data on the relation of thermoelectric voltage to temperature coefficient of resistance between 0 and 100 °C.

The effects of impurities on the electrical properties of platinum at high temperatures are summarized in table 5 and figure 12, both of which are derived from Cochrane's research [38].

## 7. RECOMMENDATIONS FOR USAGE

SRM 1967 is intended for use as a standard reference thermoelement from 77K (-196 °C) up to 2040 K (1767 °C). However, great caution must be exercised if it is to be used above 1200 °C. The material may be used as (1) a reference thermoelement for calibration of various thermocouple materials; (2) the negative leg of the standard thermocouple (Type S) in the IPTS-68 defined temperature range from 630.74 to 1064.43 °C; or (3) the negative leg of Type S or Type R thermocouples in their temperature range from -50 °C to near the melting point of platinum.

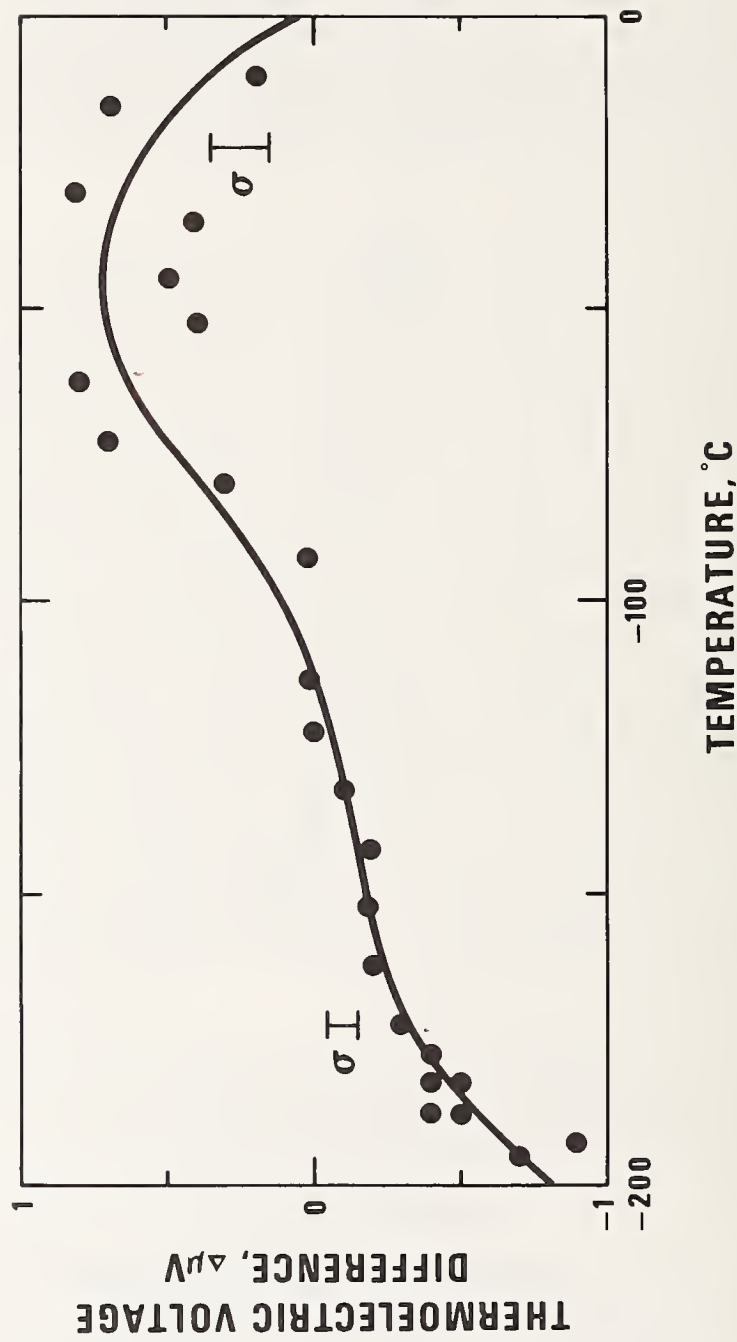


Fig. 11. Deviation of thermoelectric voltage for two platinum thermoelements at low temperatures.

Table 5. Effects of impurities on the electrical properties of platinum.

<u>Effect on Voltage, <math>\mu\text{V}/\text{ppm}</math><sup>1</sup></u>			<u>Effect on Resistance, <math>10^{-6}/\text{ppm}</math><sup>2</sup></u>	
<u>Element</u>	<u>Weight</u>	<u>Atomic</u>	<u>Weight</u>	<u>Atomic</u>
Ir	0.350	0.344	0.200	0.197
Pd	.069	.038	.100	.054
Rh	.200	.106	.090	.047
Ag	.025	.014	.150	.083
Cu	.115	.037	.349	.114
Fe	2.300	.658	1.280	.366
Ni	0.499	.150	0.160	.048
Cr	4.041	1.077	3.250	.866
Mn	0.322	0.091	0.212	.060
Pb	2.999	3.178	.900	.956
Au	-0.070	-0.071	.070	.071
Ru	1.099	.570	.250	.129
Si	1.173	.169	.550	.079
Co	0.161	.049		
Os	1.955	1.906		
Ta	0.920	0.853		
Re	3.680	3.513		
W	2.645	2.493		
Mo	3.680	1.810		

<sup>1</sup> Change in microvolts with the reference junction at 0 °C and the test junction at 1200 °C.

<sup>2</sup> Change in resistivity coefficient, alpha, the temperature coefficient of resistance  $\alpha = (R(100\text{ °C}) - R(0\text{ °C}))/100 R(0\text{ °C})$ .

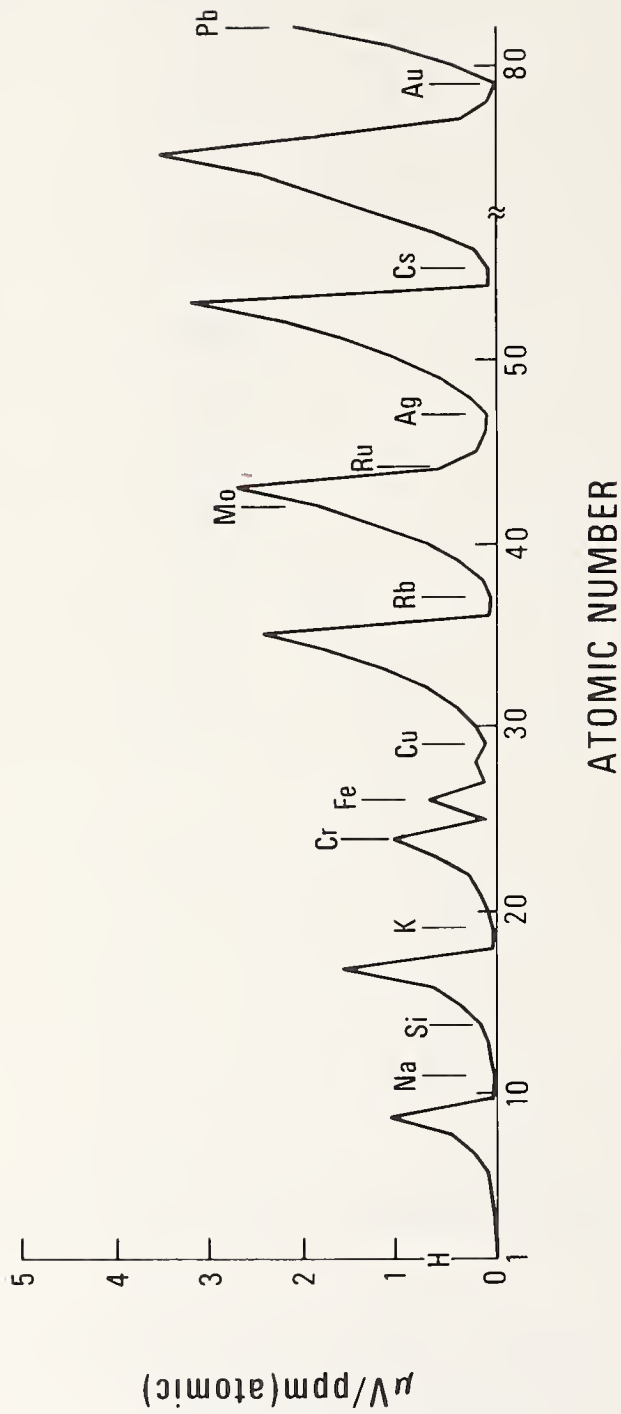


Fig. 12. The specific effect of impurities on the high temperature thermoelectric voltage of platinum.

The proper usage of platinum as a thermoelectric standard requires (1) the availability of highly-characterized, high-purity material; (2) careful annealing and handling techniques for the material; and (3) an accurate experimental methodology. The first requirement is satisfied by the certification of this SRM 1967. The second and third requirements are discussed next.

### 7.1. Annealing and handling

The recommended procedure for preparing a Pt-67 standard reference wire is:

1. Clean with ethanol and air dry.
2. Suspend wire in clean, dust-free cabinet and connect to a current source.
3. Continuously increase the current until the wire is at about 1373 K.
4. Maintain this temperature for 10 minutes.
5. Slowly decrease the current until the temperature of the wire is just below incandescence, hold for 60 minutes and slowly cool to room temperature.
6. Care should be taken at all times to avoid unnecessary mechanical stresses of the wire. If the platinum is to be used at high temperature, use special gloves or paper padding while handling.
7. High-purity sintered alumina tubing is recommended for insulating and protecting the platinum wire during use at high temperatures. After assembling the wire in an insulating tube, reanneal the assembly in a furnace for 60 minutes at 1100°C, followed by slow cooling to room temperature.

If the wire is to be used above 1100 °C, then the annealing temperature should be correspondingly raised. Bedford, et al. [8] recommend holding the wire at the higher temperature for 30 minutes, then reannealing the experimental thermocouple assembly in protection tubes at 1100 °C for 60 minutes. The other steps remain the same.

### 7.2. Experimental methodology

For any temperature range, the general principles discussed by Roeser and Lonberger [13] should be observed. For cryogenic usage, Hust, et al. [16] describe methods for thermocouple thermometry; for high temperatures, the problems and precautions described by Jones [33] and McLaren and Murdock [34] should be carefully considered.

It should be emphasized again that temperature measurements determined with Type S thermocouples in the temperature range from 630.74 to 1064.43 °C are based on the defined quadratic thermoelectric behavior imposed by the IPTS-68. There are probably significant (0.5 °C) differences between the IPTS-68 scale and best estimates of thermodynamic temperatures in this temperature range. For accurate thermophysical measurements, results should be presented in terms of the IPTS-68, but corrections based on the work of Evans and Wood [32] or Quinn, et al. [28] may be necessary to obtain smoothly varying property values.

Platinum thermoelements and Types S, R, or B thermocouples have environmental restrictions when used at high temperatures. They should not be used in reducing atmospheres, nor in those containing metallic vapor (such as lead or zinc), nonmetallic vapors (such as arsenic, phosphorous, or sulfur) or easily reduced oxides, unless suitably protected with non-metallic protecting tubes. They should never be inserted directly into a metallic primary tube.

Platinum thermoelements that conform closely to the high temperature values may not necessarily conform closely at cryogenic temperatures, especially near 77 K. If they are to be used for accurate measurements both above and below 0 °C, then the materials should be calibrated against carefully maintained Pt-67 specimens in both temperature ranges.

### 7.3. Availability

SRM 1967 (Pt-67), issued as 24 AWG wire (0.51 mm diam.) in multiples of 1 meter length up to a maximum of 3 meters length, may be ordered from the Office of Standard Reference Materials, Chemistry Building, National Bureau of Standards, Washington, D.C. 20234. (Longer continuous lengths in multiples of 3 meters can be obtained by special order to the OSRM.)

## 8. ACKNOWLEDGMENTS

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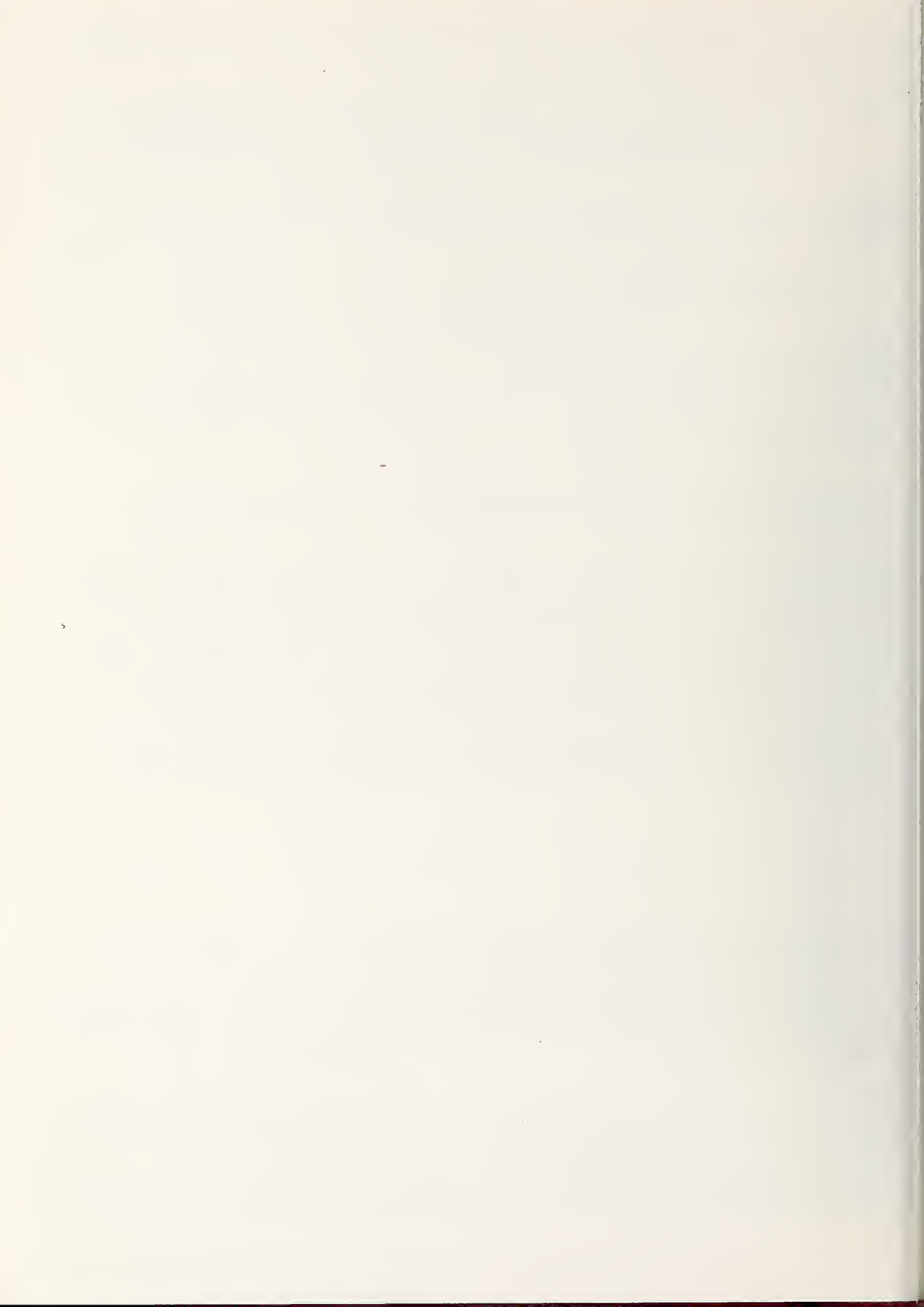
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<b>ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)</b> <p>Industry-wide standardization of thermocouple wire depends in part on thermoelectric comparisons of commercial wires to a standard. In this paper we describe a thermoelectric standard, designated Pt-67, which is available in wire form as a Standard Reference Material (SRM 1967). High purity platinum meets the requirements of a thermoelectric reference material for temperatures from 77K (-197 °C) up to 2040K (1767 °C). Thermoelectric voltages, residual resistance ratios, temperature coefficients of resistance, and chemical composition are reported for a high purity, highly characterized lot of platinum that has been developed as a thermoelectric standard, Pt-67. A review of the historical development of the material is followed by characterization data on the material and descriptions of the cryogenic and high temperature apparatus. The important effects of impurities are also described. Recommendations and precautions for usage of the reference material conclude the discussion.</p>			
<b>KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)</b> Chemical composition; effect of imperfections; high purity platinum; high temperature thermoelectric measurements; low temperature thermoelectric measurements; platinum; Pt 67; residual resistivity ratio; Standard Reference Material; temperature coefficient of resistors; thermocouple; thermoelectric standard; thermoelectric voltage.			
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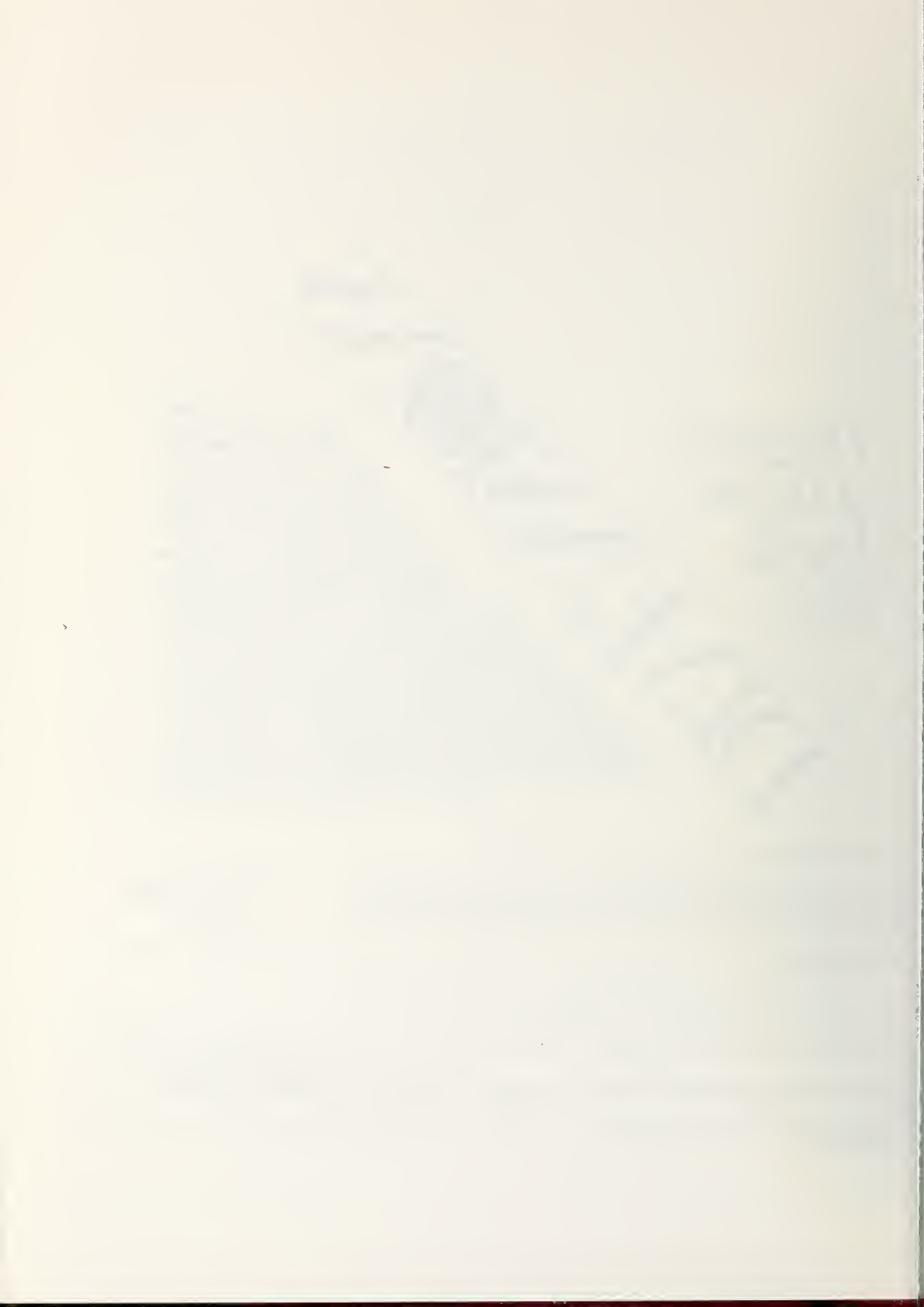
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