DEPARTMENT OF COMMERCE

CIRCULAR

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 66

STANDARD SAMPLES FOR THERMOMETRIC FIXED POINTS

[1st Edition]
Issued July 25, 1917

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CONTENTS

I. INTRODUCTION

In response to many urgent requests for a concrete realization of a series of standard temperatures, which would be available to anyone anywhere for the standardization of pyrometers and for the reproduction of the standard scale of temperature for use in laboratory and industrial works, the Bureau has had prepared a series of pure metals, of which it has made chemical analyses as a check on the degree of purity realized, together with exact determinations of the respective melting or freezing points.

The melting and freezing points of pure substances, such as are here considered, are identical. Impure substances, unless they are eutectics, do not have definite freezing or melting points. Since it will be more convenient in most instances to determine the freezing points of these standard samples, the term "freezing point" will be used in this circular instead of the longer expression "freezing or melting point."

It was decided to secure metals of the highest purity and of American manufacture, and this was accomplished in a more satisfactory manner than could have been anticipated. In the preparation of these temperature standards the Bureau has had the

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hearty cooperation of several American companies, which have succeeded in producing the metals required for the purposes at hand in at least as high a state of purity as could have been obtained anywhere.

II. SAMPLES AVAILABLE

In this, the first Bureau circular relating to the subject, are described the samples of tin, zinc, aluminum, and copper which are now available for distribution as standard temperature samples. Preparations are under way to add samples of pure lead to this list. As soon as opportunity permits, palladium and platinum samples in the form of wires will be added to serve for the reproduction of the temperature scale up to 1755° C, and it is expected that others will be added as the demand for them may arise. Pure samples of naphthalene, benzophenone, and sulphur would serve, by means of their boiling points, taken under carefully specified conditions, as excellent standard temperature samples for the reproduction of the lower range (to 450° C) of the temperature scale with the highest attainable accuracy.

III. PREPARATION OF THE METALS

Each company that undertook the responsibility of furnishing a metal for use as standard samples exercised most painstaking care to produce the best possible product as to purity and uniformity. A representative of the Bureau witnessed the actual preparation of each metal.

1. **Tin.**—The tin was furnished by the American Smelting & Refining Co. under the immediate personal supervision of Mr. Whitehead, its metallurgist.

The tin was produced from Bolivian ores in the company's experimental electrolytic plant at Maurer, N. J. The metal furnished was a second electrolytic deposit from anodes of high-grade electrolytic tin. The cathode plates thus obtained were melted all together in one operation in a graphitized iron pot, the tin surfaces being kept clean, and then cast to size in iron molds, thus furnishing the samples in form for distribution.

2. **Zinc.**—The zinc was from the New Jersey Zinc Co. and was part of a specially made lot prepared for the Bureau for special experimental purposes as well as for use as standard temperature samples. It was prepared under the direct personal supervision of G. C. Stone and G. Rigg at the company's Palmerton plant.

The following extract is taken from a report of the New Jersey Zinc Co. on the preparation of pure zinc:

The metal was obtained by the redistillation of Horse Head spelter, and the work was carried out in a one-muffle furnace in the experimental building of the research department. The furnace consisted merely of a firebox adapted to burn No. 2 Buck coal with an undergrate blast and carrying over the fire two regular 5-foot spelter muffles, one above the other. The lower of the two muffles served merely as a "cannon" to protect the upper or working muffle from extremes of temperature. The upper muffle was placed so that its mouth lay about 4 inches higher than the butt, in order to increase its working capacity. The condenser used was a regular spelter condenser having a dam placed at the back, filling slightly more than half of the rear opening. The purpose of this dam was to prevent metal from the retort from runnung directly into the condenser, as the normal working charge in the retort is large enough to bring the level of the metal above the bottom of the condenser.

The method of operation is as follows: The muffle is thoroughly burned in place and the temperature of the furnace is lowered to about 1100° C, and approximately 250 pounds of spelter is charged into the muffle. The condenser is then loamed into place, and before the metal has time to melt its nose is plugged with damp anthracite dust coal. A small hole is spiessed in the top of this coal plug. After the metal has begun to volatilize the temperature is regulated so that zinc vapors are always just ready to emerge from this hole, but do not do so if the temperature is properly regulated. The emission of a flame 2 to 3 inches long for a period of 10 minutes has a decided effect on the lead content of the distilled spelter.

The metal is drawn every three hours, and after each draw a weight of Horse Head spelter is charged which is approximately equal to the weight of the draw plus the blue powder made. By this means the metal in the bath is kept at a nearly constant weight of about 250 pounds. When the lead in the redistilled spelter rises to 0.01 per cent the metal in the muffle is replaced by fresh Horse Head spelter.

All of the spelter sent to the Bureau of Standards was made as outlined above. No metal actually assaying 0.01 per cent Pb was used, however, and the metal remelted and cast into the required shapes was very soft and "dead," and its fracture exhibited very beautiful crystallization.

The metal was then melted in a graphite pot and ladled out with graphite ladle into graphitized iron molds; the piped portions were then cut off, leaving the samples in the form of cylinders 10 by 1 cm, suitable for distribution.

3. **Aluminum.**—This metal was furnished by the Aluminum Co. of America and was produced in its Niagara works by its regular process, with especial care taken to get as high aluminum content as possible. The preparation of the samples was carried out under the direction of E. Blough, the chief chemist of the company.

The cylinders constituting the samples were cast from two batches of aluminum billets, the analyses made by the Aluminum Co. of America being as follows in percentages:

Pot No.	Al	Cu	Si	Fe	Weight
					Pounds
38	99.71	0.02	0.12	0.15	171
19	99.70	.01	.17	.12	145

The billets were cut into pieces before introducing into the melting crucibles, and in this way parts of each batch were introduced at the same time.

The melting was in graphite crucibles heated in crucible furnaces fired with natural gas and compressed air. The crucible was tightly closed during melting by a graphite cover. About 50 pounds of metal was melted for each pouring, the time of melting being about 45 minutes.

After removing the crucible from the furnace the scum was removed from the surface of the molten metal by means of a graphite ladle. The molten metal was poured into a graphite ladle and then into a graphite mold having nine compartments of the size of the finished cylinder. The cylinders were removed from the graphite mold as soon as they were sufficiently chilled for handling and placed on the floor to cool.

Great care was exercised in the melting and pouring of the metal. It was not in contact with iron during any stage of the process, and the only possible contamination from silica was from the graphite crucibles and ladles. These, however, were new and and no dissolving action was observed.

4. **Copper.**—This metal was an electrolytic product furnished by the Raritan Copper Works and was prepared under the personal supervision of F. L. Antisell, assistant superintendent of its Perth Amboy plant. It was considered advisable not to remelt this copper, in order to avoid the introduction of oxides and other impurities. The samples were obtained by forming an extra heavy electrolytic deposit which was stripped from the cathodes and then cut to size with shears.

IV. CHEMICAL ANALYSES OF THE METALS

All analyses were made by the Bureau on composite samples made up of material taken from portions covering the whole lot. The several companies furnishing the metals each submitted statements, previous to manufacture, of the purity they expected to obtain. This expectation of purity was substantially fulfilled in each case. All of the samples were of practically uniform analysis throughout.

1. **Tin.**—The American Smelting & Refining Co. stated its ability to furnish a tin 99.99 per cent fine; the Bureau's analyses show 99.988 per cent tin and indicate that the material is uniform in composition. The product would undoubtedly have come lower in lead, the principal impurity, if the tin cathode plates (of

once-deposited metal) used for supporting the second and final deposit had been stripped and discarded.

The following is the analysis of the metal from samples as cast:

Element sought	Per cent found	Weight of sample analyzed
		Grams
Lead	0.007	75
Copper	.003	75
Iron	.002	75
Antimony	Not detected	10
Arsenic	Trace	10
Sulphur	Trace	10
Tin by difference	99.988	.....
Other elements not looked for.		

The best grades of Banca tin average 99.94 to 99.97 tin.

This electrolytic tin was of such remarkable purity that it was thought to be of sufficient interest to examine it spectroscopically to see whether the presence of minute traces of other elements could be detected. The spectroscopic examination confirmed the presence of copper and lead, did not definitely indicate the presence of iron, and gave no indication of cadmium, zinc, or antimony.

2. **Zinc.**—The New Jersey Zinc Co. expected to produce a metal containing not over 0.04 per cent total impurities, and its product as remelted and cast into samples is much better than this; it analyzes 99.993 per cent zinc, as shown below. There is included for comparison a simultaneous analysis of highest grade Kahlbaum zinc.

CHEMICAL ANALYSES OF ZINC SAMPLES

Element sought	New Jersey Zinc Co.'s redistilled Horse Head spelter, per cent found	C. A. F. Kahlbaum zinc, per cent found	Weight of sample analyzed
			Grams
Iron	0.005	0.001	250
Lead	.0004	.021	250
Cadmium	.0018	.021	250
Arsenic	Trace	Trace	50
Antimony	Not detected	Not detected	50
Tin	Not detected	Not detected	250
Sulphur	Trace	Trace	10
Zinc by difference	99.993	99.957	.....
Other elements not looked for.			

An analysis by the research department of the New Jersey Zinc Co., also on the cast samples, gave 0.004 per cent Fe, less than 0.005 per cent Pb, and less than 0.0001 per cent As.

This zinc dissolves readily in dilute acids, wherein it differs markedly from the Bertha brand zinc. It was also found to dissolve somewhat more readily than a specimen of Kahlbaum zinc. When the Horse Head redistilled zinc is immersed in acid, some of the contained iron appears on the surface of the zinc. This iron dissolves readily in dilute acids when not in contact with the zinc.

3. **Aluminum.**—This is the least pure of the metals of this series, it being impracticable, apparently, to manufacture aluminum in considerable quantity of the high degree of purity attained in the other metals. The Aluminum Co. of America expected to be able to furnish aluminum of 99.70 per cent purity, and the Bureau's analysis of the remelted cast samples shows 99.66 per cent Aluminum, as follows:

CHEMICAL ANALYSIS OF ALUMINUM SAMPLES

Element sought	Per cent found	Weight of sample analyzed
		Grams
Iron	0.18	2.5
Silicon	.15	2.5
Copper	.004	10.0
Manganese	Trace.	1.0
Carbon	.01	5.0
Cobalt and nickel	Not detected.	.....
Aluminum by difference	99.66	.....
Other elements not looked for.		

4. **Copper.**—The Raritan Copper Co. undertook to furnish electrolytic copper of 99.96 purity or better. The actual metal furnished is 99.987 copper, as shown by the Bureau's analysis given below:

CHEMICAL ANALYSIS OF COPPER

Element sought	Per cent found	Weight of sample analyzed
		Grams
Antimony	0.004	50
Arsenic	.0026	50
Sulphur	.0026	10
Copper	99.987	5
Other elements not looked for.		

Microscopic examination did not reveal the presence of oxygen present as cuprous oxide in the copper.

In general this material is very uniform. In some of the bars a very slight amount of electrolyte has been included, as shown by the blue color. This, however, is extremely rare and small in amount.

V. FREEZING POINTS AND TEMPERATURE SCALE

The freezing points of these standard pyrometic samples were determined by means of electrical-resistance thermometers of pure platinum calibrated at 0°, 100°, and 444.6° C, the freezing and boiling points of water and the boiling point of sulphur, respectively.

Altogether, four separate platinum thermometers were used with two separate precision Wheatstone bridges, modified to permit measurement of potential-terminal resistances. A series of both freezing and melting points were taken of at least two samples of each metal. The apparatus and methods of measurement have been described elsewhere.[1]

This temperature scale, given by the resistance thermometer of pure platinum, within the range defined by this series of metals (0 to 1100° C), reproduces the standard scale of temperatures generally in use as closely as it can be determined.

The value of the freezing point for any particular sample of metal, representing the purity and product of a single manufacturing operation, may not be identical with the freezing point of the metal prepared at another time. *The actual value to be used for the freezing point will be given by a certificate furnished with each sample.*

In the following table are given the values of the freezing points of the first lots of the first series of metals now being issued:

Metal	Freezing point	Purity
	°C	Per cent
Tin	231.8_8	99.988
Zinc	419.4_4	99.993
Aluminum	658.6_8	99.66
Copper	1083.0	99.987

The freezing point of the Kahlbaum zinc, the analysis of which is given in the preceding section, is 419.30° C.

[1] Waidner and Burgess, Bull. Bureau of Standards, 6, pp. 149–230; 1910 (Scientific Paper No. 124).

VI. USES OF STANDARD TEMPERATURE SAMPLES

These samples may be used to reproduce the standard scale of temperature with the highest accuracy required in laboratory investigations or in the standardization of pyrometers. They are primarily intended for the standardization of rare-metal thermocouples and of platinum resistance thermometers, although for the latter purpose the ice, steam, and sulphur boiling-point calibration is perhaps preferable if the thermometer coil is of pure platinum.

Various types of interpolation formulæ for the thermocouples and convenient methods of computation have been described in several publications.[2]

These samples are obviously not intended for the calibration of heavy base-metal thermocouples, which would require great depth of immersion in the metal, and hence large amounts of metal, to eliminate the effects of heat conduction along the heavy leads and protecting tubes.

Where heavy base-metal couples have to be standardized, this may be done by direct comparison, in an electric furnace, with a rare-metal couple that has been standardized by use of these samples. Or a stock of commercially pure metals may be purchased at comparatively small cost for use as secondary standard samples, the freezing points of these commercial samples being determined by a rare-metal couple that has been standardized by use of the certified samples or by some standardizing laboratory.

A convenient fixed point for the standardization of pyrometers is also furnished by the freezing point of sodium chloride (801° C). The salt may be melted in a nickel crucible.

The copper sample may be used to obtain a standardization temperature for optical pyrometers by immersing a closed-end thin graphite tube in the metal and observing the radiation emitted by the bottom of this tube when the metal is freezing. With some optical pyrometers, which do not absorb too much light, aluminum can be used in this way to define a lower calibration point.

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[2] Bureau of Standards Circular No. 7, 5th ed., 1913; Burgess and Le Chatelier, The Measurement of High Temperatures, 3d ed., pp. 108–115 (pub. by John Wiley & Sons, New York, 1912); Day and Sosman, The Nitrogen Thermometer from Zinc to Palladium, Am. Jour. of Science, IV—29, p. 93, 1910; Sosman, The Platinum Rhodium Thermoelement from 0° to 1755°, Am. Jour. of Science, IV—30, p. 1, 1910; L. H. Adams, Calibration Tables for Thermoelements, Jour. Am. Chem. Soc., 36, p. 65, 1914; Foote, Note on Cold-Junction Corrections for Thermocouples, Bull. Bureau of Standards, 9, p. 563, 1913 (Scientific Paper No. 202).

VII. PRECAUTIONS IN USE OF STANDARD SAMPLES

In the process of reducing these metal samples to smaller dimensions, either by sawing or cutting, for filling into the crucible, care should be exercised to keep the metal clean. The total impurity in a zinc sample is only about 25 mg and this amount might easily be doubled by careless handling.

The metal samples should be melted in clean graphite crucibles, preferably provided with covers having central holes to admit the pyrometer protecting tubes. A crucible of capacity somewhat greater than 50 cm^3 and of elongated form is most satisfactory. Crucibles free from contaminating impurities may be turned from Acheson graphite rods. Such crucibles, although soft, may be used for a long time in an electric furnace, if carefully protected from air when used above 500° C.

Electric furnaces are cleaner and more convenient in manipulation than gas or oil furnaces, although the latter may be satisfactorily used.

The tin and zinc may be melted without special precautions against oxidation, although it is better not to overheat, and the exposed surface of the metal can be protected to advantage by powdered graphite.

Aluminum is readily oxidized and contaminated and should be melted under graphite in crucibles free from silica.

It is difficult to melt copper without some oxidation occurring, which may be in part obviated by protecting the surface with graphite powder. The oxidation of the copper gradually lowers its freezing point, and this may go on until 1063° C, the Cu-CuO eutectic point, is reached.

As the oxidation of the copper proceeds, the freezing curve (time-temperature curve), which with pure material shows sudden changes of direction at the beginning and at the end of freezing, alters its form. With slight oxidation, the principal change observed is that the end of freezing is not sharply defined, although the temperature at the beginning of freezing is only slightly lower than the freezing point of pure copper. With further oxidation the initial freezing point is lowered, and the conclusion of freezing becomes more and more indefinite. The presence of copper oxide in copper can be detected microscopically, but the interpretation of the appearance observed under the microscope would require a good metallographic equipment and experience.

The oxides of tin, zinc, and aluminum have little if any effect on the melting (or freezing) point of these metals, since these oxides are practically insoluble in their metals.

Porcelain or fused-silica tubes may be used for protecting the resistance thermometers or thermocouples in tin, zinc, and copper, but in aluminum it is necessary to protect the metal from the pyrometer inclosing tube. This may be done by inclosing the latter in a closely-fitting thin tube of Acheson graphite. The smaller the diameter of the pyrometer tube the less liability will there be to error due to heat conduction. The user must assure himself that the junction of the thermocouple or the coil of the resistance thermometer is immersed to a sufficient depth in the crucible to insure that it is actually at the temperature of the freezing metal. A criterion to determine whether the depth of immersion is sufficient is to raise the junction or coil by an appreciable distance; if there is no resulting apparent decrease in the temperature indicated, the depth of immersion is sufficient.

The pyrometer tube should be removed from the metal after taking an observation; otherwise the tube may be broken on cooling or on reheating from lower temperatures. The tube will invariably be broken on heating if left in zinc. If the same inclosing tube is used in more than one metal, care must be taken, by washing with acid or otherwise, to always insert a clean tube in each metal.

VIII. DISTRIBUTION AND PRICES OF SAMPLES

Requests for standard temperature samples should be addressed "Director, Bureau of Standards, Washington, D. C." All fees are payable in advance. The sender may remit by personal check or by United States postal money order.

The tin, zinc, and copper samples are furnished in quantities of about 50 cm^3 each, the aluminum sample about 80 cm^3, inclosed in pasteboard cases. Each sample is accompanied by a certificate which gives the melting point as determined from samples of the same lot; also by a copy of this circular.

The samples may be ordered by number, as follows:

Sample No.	Metal	Price
42	Tin	$2.00
43	Zinc	2.00
44	Aluminum	2.00
45	Copper	2.00

A discount of 10 per cent is allowed on lots of four of one or different metals.

S. W. STRATTON,
Director.

Approved:
WILLIAM C. REDFIELD,
Secretary.