

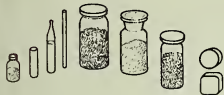
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Standard Reference Materials:

**PREPARATION OF NBS
WHITE CAST IRON SPECTROCHEMICAL
STANDARDS**



**U.S. Department of Commerce
National Bureau of Standards**

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Standard Reference Materials:

Preparation of NBS White Cast Iron Spectrochemical Standards

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Washington, D.C.



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PREFACE

Within the framework of the NBS Institute for Materials Research the area of standard reference materials is a broad and important one, including the preparation, characterization and distribution of a wide variety of materials in such diverse fields as metallurgy, polymers and inorganic materials. In carrying out such a program there is much interaction with representatives of industry and science, beginning with discussions as to which primary standard materials will do most to advance technology, the furnishing of materials and fabrication of samples, and the characterization and certification of the materials by cooperative efforts. The many groups participating in a standards program are very interested in detailed information on specific aspects of the program -- but to date there has been no publication outlet for such written discussions.

To meet this need, NBS Miscellaneous Publication 260 has been reserved for a series of papers in the general area of "standard reference materials". This series will present the results of studies and investigations undertaken within the Institute for Materials Research with emphasis on the preparation and characterization of standard reference materials. This subject-oriented series will provide a means for rapid dissemination of this detailed information and we hope will stimulate the use of standard reference materials in science and industry.

OTHER NBS PUBLICATIONS OF INTEREST

NBS Miscellaneous Publication 241, Standard Materials Issued by the National Bureau of Standards: A Descriptive List with Prices, March 1962. 30 cents.

NBS Miscellaneous Publication 250, Calibration and Test Services of the National Bureau of Standards, November 1963. 70 cents.

Send orders with remittance to: Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 20402. Remittances from foreign countries should include an additional one-fourth of the purchase price for postage.

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PREPARATION OF NBS WHITE CAST IRON SPECTROCHEMICAL STANDARDS

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Several methods have been investigated for the preparation of cast iron spectrochemical standards and a satisfactory procedure has been devised. The method involves casting the molten metal into a grid type of mold on a massive water-cooled copper plate. The method has been applied to the preparation of eight NBS white cast iron spectrochemical standards containing a graded concentration range for some 20 elements, of which the following 10 initially have been certified: C, Mn, P, S, Si, Cu, Ni, Cr, V, and Mo. Details of the planning and preparation are given with particular emphasis on the problems peculiar to standards for cast materials.

1. INTRODUCTION

Cast iron may be described generally as an alloy of iron and carbon where the carbon content is between 1.7 and 4.5 percent. This is more carbon than can be retained in austenite at the eutectic temperature; hence on slow cooling the casting normally will exhibit a matrix of pearlite with many graphite flakes dispersed throughout. Such material is known as gray iron and was so named because of the characteristic "gray" fracture imparted by the graphite flakes. The tonnage production of gray iron exceeds that of all other

cast metals combined. Also included in the general term "cast iron" are pig irons, white irons, chilled irons, and malleable irons.

The rapid methods of spectrochemical analysis have been employed widely in the cast iron industry for the determination of most metallic constituents. In recent years, however, developments in spectrochemical instrumentation, particularly the vacuum emission spectrometer, made possible the complete analysis of cast irons including determinations for carbon, phosphorus, and sulfur. This markedly extended the use of spectrochemical analysis in the cast iron field. Also of significant interest has been the increasing application of x-ray spectrochemical methods for the analysis of materials such as cast iron.

The major limitation to quantitative spectrochemical analysis is that the methods are not absolute, but are dependent on the technique of comparison with samples of known composition, referred to as standard samples. Thus the problem of calibration is of paramount importance to the accuracy of spectrochemical analysis. Standard samples must not only be of high homogeneity and have accurate values assigned to them, but also extreme caution must be exercised in matching the standards and the unknown samples with respect to all variables such as size, shape, composition, and metallurgical condition.

The acute need by both industry and government for

reliable and accurate cast iron spectrochemical standards was made clear to the National Bureau of Standards in the early 1950's by surveys and communications; and in 1955 an active program for the preparation of suitable standards was initiated.

The main purposes of this paper are to describe the development of a satisfactory method of preparation for cast iron standards and to evaluate the application of this method to a set of eight prepared NBS spectrochemical standards.

This work was supported in part by the American Iron and Steel Institute.

2. CONSIDERATION FOR PREPARATION

The preparation of spectrochemical standard samples to be provided in the "as cast" condition presents several difficulties not encountered in those which can be provided in the wrought condition. For wrought standards, non-homogeneous portions can be determined and discarded prior to working to the final size. Equally significant is the fact that the final homogeneity in the wrought standard can be improved markedly over that of the selected material by appropriate working and heat-treating operations [1]. For "as cast" standards, the required chemical homogeneity and desired metallurgical structure are obtained solely through metal pouring and casting procedures.

Additional difficulties in the preparation of cast iron standards over most other cast materials are encountered

because of the variety of complex metallurgical structures which may be formed on the solidification of the cast iron from the molten state, and which may markedly influence the spectrochemical results. The final metallurgical structure depends primarily on the composition, pouring temperature, and rate of cooling.

3. TYPE OF CAST IRON FOR STANDARDS

Since gray iron is by far the most widely used type of cast iron, it commanded initial consideration. On investigation at NBS and elsewhere, however, it was shown that the graphite flakes, in terms of amount, size, shape, and distribution, had a pronounced effect on the volatility rates in the determination of some elements by optical emission analysis.

In white cast iron virtually all of the carbon exists in the combined form and there is essentially no free graphite. Although limited in engineering applications, the white cast iron was considered to be the most advantageous material for the spectrochemical standards for the following reasons. (1) It would provide a uniform metallurgical structure for a series of standards to cover wide concentration ranges for the elements of interest. (2) It would offer a casting material that could be prepared to provide the requisite homogeneity of chemical composition. (3) Investigation had shown that test samples with an induced white structure could be prepared in the foundry for most types of

iron; these could thus be analyzed directly relative to the white iron standards. The white structure can be induced in at least a portion of the test samples either by using a rapid chill-casting procedure or by making certain additions known to promote whiteness, such as tellurium or bismuth, or by a combination of both, to the test ladle or mold. (4) Finally, the white cast iron provides the opportunity to make the important determination of total carbon by vacuum optical emission analysis, which would not be possible if much of the carbon was present in an uncombined form.

4. CHEMICAL COMPOSITIONS

In addition to those elements which may be considered the main components of an alloy, modern metallurgy is most intimately involved with the effects of minute amounts of other elements. These may be impurities inherited from the raw materials or they may be picked up from furnace linings, crucibles, etc. In any event, most contaminants are deleterious to the final alloy. However, trace quantities of some elements, not normally impurities, may be added deliberately to enhance the alloy performance.

Of further concern to the chemical composition requirements with respect to trace elements is the fact that the material sources and the processing methods may vary appreciably among the producers for a particular alloy. As a consequence, each may have his particular problems with respect to control of these elements. Thus the compilation

of essential plus desired elements into a prospective table of composition for most standards is somewhat akin to a roll call of an appreciable segment of the periodic table.

The results of a survey conducted in 1950 by ASTM Committee E-2 on Emission Spectroscopy revealed that at that time 13 elements were required for inclusion in proposed cast iron spectrochemical standards. Also significant was the realization that eight individual standards would be required to cover the wide ranges of concentration for most of the desired elements. In 1955 the NBS, in cooperation with the cast iron industry, planned the chemical compositions for eight white cast iron spectrochemical standards. The final compositions adopted by NBS and accepted by industry are shown in table 1. As can be seen, the proposed standards were planned to contain a concentration range for 21 elements (and iron). To provide for general application of the standards, five commercial cast iron compositions were chosen: piston ring, wear plate, die, brake drum, and mold. To these, three special compositions were added to provide for the required wide concentration ranges of the contained elements.

The balancing of the eight compositions to promote a white structure required careful study [2]. For example, the silicon content is the principal factor in controlling depth of chill. Chromium and vanadium are strong carbide formers and hence markedly promote the chilling properties.

Table 1. Planned Compositions of Eight Proposed
NBS White Cast Iron Spectrochemical Standards

Number Designation Element	1	2	3	4	5	6 7 8		
	Piston Ring	Wear Plate	Die	Brake Drum	Mold	Modified		
	%	%	%	%	%	A	B	C
C	3.8	2.5	3.0	3.3	3.4	4.0	2.0	3.1
Mn	0.6	0.3	0.9	0.75	1.2	1.5	0.5	1.0
P	.4	.6	.1	.2	0.05	0.3	.8	0.01
S	.07	.04	.02	.2	.1	.05	.03	.02
Si	2.8	.9	1.9	1.5	3.2	2.7	.5	2.0
Cu	0.7	.05	0.15	0.4	0.2	1.5	.5	1.0
Ni	.05	3.0	2.2	1.3	.03	0.1	.2	0.5
Cr	.5	1.4	0.8	0.2	.1	2.0	.03	.08
V	.15	0.005	.02	.03	.25	0.1	.05	.07
Mo	.6	1.5	.9	.3	.15	.03	.01	.02
Ti	.2	0.1	.15	.02	.35	.002	.01	.005
As	.005	.01	.02	.05	.07	.1	.15	.2
Sb	.3	.2	.1	.1	.05	.02	.01	.005
Sn	.005	.02	.07	.1	.02	.04	.01	.15
Co	.005	.1	.05	.02	.03	.015	.005	.01
Te	.02	.01	.005	.03	.05	.06	.005	.025
B	.002	.02	.1	.05	.0007	.001	.01	.005
Bi	.02	.03	.04	.005	.01	.005	.025	.05
Pb	--- ^a	---	.005	.01	.002	.02	.005	.02
Zr	---	---	.04	.02	.005	.1	.01	.15
Al	---	---	---	---	---	---	---	---

a
Dashes indicate that no addition for this element was planned. For aluminum it was anticipated that a concentration range of about 0.01 to 0.1 percent would be obtained as a result of this element being present in several of the planned master alloy additions.

Phosphorus and nickel reduce the depth of chill. Manganese and sulfur usually form manganese sulfide, and if balanced with respect to each other in the proportions added, have little effect on the chill. In the absence of enough manganese, however, sulfur has a marked stabilizing action on the cementite and promotes chill.

In the cast iron industry, the tendency to graphitize often is expressed as the "carbon equivalent", an empirical relationship of the total carbon, silicon, and phosphorus content expressed by the formula: $CE = \%TC + 0.3 (\%Si + \%P)$. Most gray iron foundries prefer to hold their CE within the range of 3.9 to 4.3. When the eight planned compositions are examined in the light of their carbon equivalents, as shown below, it is evident that on this basis, several of the

Carbon Equivalents

Number	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
Value	4.9	3.0	3.7	3.9	4.5	5.0	2.4	3.8

compositions have considerable tendency toward graphitizing. Admittedly, this crude calculation does not take into account the other elements present in the proposed standards; however, it appeared desirable to add the powerful carbide stabilizers, tellurium and bismuth, to ensure heavy chilling and also to provide a concentration range for these elements as well.

5. CASTING

Early attempts to prepare white cast iron standards included: centrifugally-cast pins (Research Laboratories of the General Motors Corp.), machine-cast bolts and centrifugally-cast large diameter pipe (American Cast Iron Pipe Co.), and unidirectionally solidified slabs cast on a copper plate (Watertown Arsenal). Although none of these were entirely successful, the results of studies at NBS on the cast slabs appeared promising; it was determined that (1) a suitable depth of chill for standards could be induced for most cast iron compositions; (2) homogeneity of both composition and structure were satisfactory, particularly near the chill-cast surfaces; and (3) samples cut from the slabs were equally suitable to both optical emission and x-ray spectrochemical methods of analysis. Because of the extreme hardness ($RC \bar{5} 60$) of the white cast irons, however, cutting the slabs to samples was found not to be economically feasible.

As a consequence of the work on the unidirectionally cast slabs, a massive water-cooled copper mold assembly was designed and constructed at NBS for unidirectional casting of a large number of white cast iron samples simultaneously.

The mold assembly, shown in figure 1, consists of a 5-ft square steel plate to the periphery of which was edge-welded a 5-in-wide steel strip to form a 5-ft annulus having a tangential outlet. Within this area another strip was edge-welded to serve as a spiral baffle from center to periphery

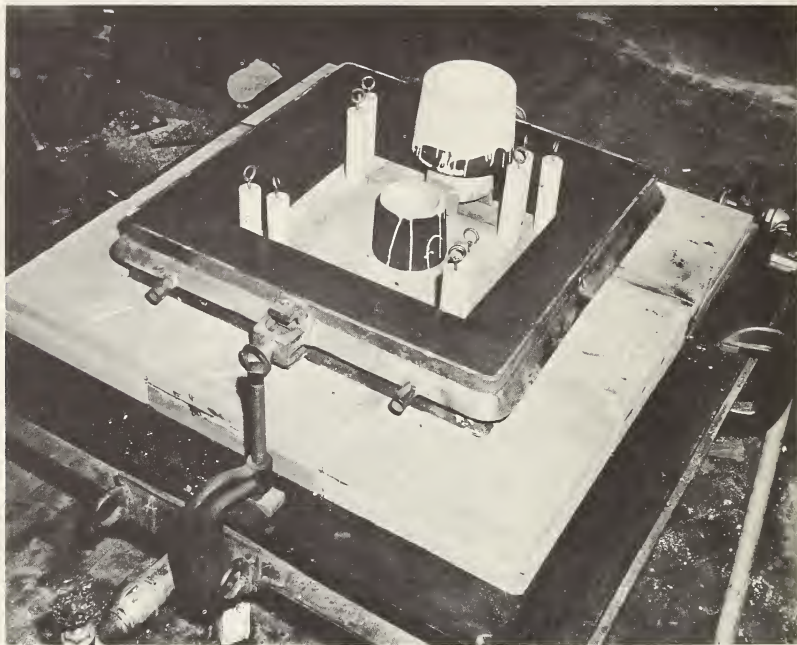


Figure 1. Water-cooled copper mold assembly designed and constructed at NBS for the preparation of white cast iron spectrochemical standards.

for water cooling. To the top of this structure was bolted a 5-ft square copper plate, 1-in. thick. The copper plate was made from oxygen-free, high conductivity (OFHC) copper. The bolts, 1 in. in diameter, also were made of OFHC copper and were threaded to extend into the copper plate about two-thirds of the thickness. A lead gasket near the periphery sealed the entire assembly to prevent water leaks.

The cooling water was supplied by a 2-in. hose line connecting the high-pressure line to the plate center; the 3-in. exit line was equipped with a valve to serve in a throttling capacity to aid in purging air from the cooling chamber.

As the result of a number of experiments with different kinds of mold wash, it was found that the best protection to the copper plate consistent with high heat transfer and least moisture difficulties was accomplished by dressing the casting surface with a very thin layer of colloidal graphite with alcohol as the carrier. The casting face was flame dried until the time of casting.

To facilitate gang-casting of the white iron samples, a grid mold assembly was mounted on top of the copper plate. Each grid mold, nine total, consisted of a three-part, pasted up and baked sand assembly (18 x 18 in. sq) which would accommodate 64 white iron blocks each separated by about 1/4 in. at the chill face. Surmounting the grid was a plate, 3/4 in. thick, having a tapered in-gate located over the center of each block cavity in the grid. The size of the in-gate was found critical in that too small an opening fostered lack of fill, cold-shuts, and spatter, while too large an opening risked damage to the cast white-iron block during subsequent break-off from its header. Good castings were obtained with in-gates having 1/2- to 5/8- in. diameter at the block cavity, and a 1/8-in. taper.

The top section of the mold consisted of a rim which formed a basin 1 7/8-in. deep above the in-gate plate, and which had a cut-out on those sides which contacted other grids to permit interflow of metal after the metal had filled the cavities, the in-gates, and to a depth of 1/4 in. in the basin.

The final casting procedure adopted may be characterized as a stoppered tun-dish technique. Essentially this consisted of providing at the top of the entire mold assembly a rammed pouring basin having stoppered holes, 2 in. diameter, one over each of the nine grid basins. Each grid basin was covered except for the stoppered opening. In the casting operation more than enough metal to fill the entire mold was poured in the basin, following which all stoppers were pulled simultaneously.

Since each grid mold accommodated 64 blocks and nine such grids were available, the casting procedure had the capability of producing 576 white cast iron samples simultaneously. However, the 10 positions at the outside four corners of the assembly were blocked off since these positions were not directly above the spiral of the water cooling. This resulted in a production capacity of 536 samples per heat.

6. MELTING

Experimental melting at NBS was carried out in a high-frequency induction furnace of 1000-lb rated capacity; however, all production heats were made at the Naval Research Laboratory* in a similar type furnace but with 350-lb rated capacity.

A listing of the materials used in melting the eight NBS white cast iron standards is given in table 2. With the exceptions of the materials for sulfur, antimony, tellurium, and bismuth, considerable experience had been gained with the listed materials previously in the preparation of eight NBS ingot iron and low-alloy steel spectrochemical standards [3].

Careful control was maintained over the melting procedures to include time, temperature, and amount and order of additions to the furnace. Table 3 shows as an example the melt log for the white cast iron brake drum standard (No. 4 in Table 1, NBS No. 1179). The total melt time for each heat was about 1 1/2 hours. In general, the expected and calculated recoveries for the elements agreed well. Table 4 illustrates the recoveries obtained for 10 of the 20 elements added. For vanadium, the high average recovery value possibly was due to

* The authors express their appreciation to L. Depue and the foundry staff at the Naval Research Laboratory both for their suggestions in the final development of the casting procedure and for permitting the use of their facilities and personnel in the production of the eight NBS cast iron spectrochemical standards.

Table 2. Materials Used in Melting NBS
White Cast Iron Standards

Element	Material Description	Purity ^a
C ^b	Electrode grade, rods 3-in. diam.	99.9+ %
Mn	Electrolytic, platelets	97 +
P	FeP, lump (24% P)	99
S	FeS, lump (36.5% S)	99
Si ^b	Metal, lump	97 +
Cu	OFHC, rod ends	99.9
Ni	Electrolytic, small plates	99.9 (Ni + Co)
Cr	Metal, lump	97 +
V	FeV, lump (48.8% V)	98.5
Mo	Metal, wire	99 +
Ti	FeTi, lump (40.0% Ti)	98.5
As	Metal, lump	99 +
Sb	Metal, lump	99 +
Sn	Metal, small ingot	99.9
Co	Metal, pellets	99 +
Te	CuTe, lump (45.5% Te)	99 +
B	FeB, small lump (11.5% B)	98.5
Bi	Metal, small lump	99.5+
Pb	Metal, shot	99 +
Zr	SiZr, small lump (41.3% Zr)	99 +
Fe ^b	Ingot iron, plate squares	99.8+ ^c

^a

Semiquantitative spectrochemical analyses were obtained on all materials to ensure positive identification and to determine the approximate concentrations of the impurities that could affect the schedule for additions.

^b

A master alloy of carbon, silicon and iron was prepared and used for the main additions of carbon and silicon. Chemical determinations showed 2.56% C and 2.72% Si.

^c

Quantitative chemical and spectrochemical determinations were made for 20 elements in the ingot iron. By difference, the iron content was 99.85%.

Table 3. Log of Melt for Brake Drum (350 lb)
Standard (NBS No. 1179) January 8, 1960

Charge: Master Alloy melting stock (305.23 lb), Ni (4.50 lb), Cu (1.00 lb).

Furnace On: 9:30 AM.

Half Melt Down: Time 10:15 AM; added C (1.88 lb), Si (none), Mn (2.68 lb).

Melt Down: Time 10:43 AM, Temp. 2500°F.

Skim: Time 10:45 AM, Temp. at end 2475°F.

Additions: (Non-volatile) Temperature to 2500°F, Time 10:46 AM, P(2.78 lb), S(1.92 lb), Cr(0.70 lb), Mo(1.05 lb), V(0.22 lb), Co(0.07 lb), Ti(0.44 lb), Zr (0.18 lb), Time: 10:48 AM, Temp. 2520°F.

Stir: Time 10:52, Temp. 2550°F.

Skim: Time 10:53, Temp. 2500°F.

Additions: (Volatile) Temperature to 2500°F, Time 10:54 AM As (0.17 lb), Sb(0.39 lb), Sn(0.39 lb). B(1.79 lb), Pb(0.88 lb), Te(0.26 lb), Bi(0.019 lb).

Stir: Temperature to 2600°F rapidly. Time 10:58 AM.

Tap: Stir in ladle Time 10:59 AM.

Mold Water on:

Sample: Two specimens

Pour: Time: 11:00 AM

Remarks

No apparent spattering of additions. 535 of 536 casting blocks filled.

Table 4. Recovery Values for 10 Elements in
the Eight NBS White Cast Iron Standards

Element	Concentration Range %	Average Recovery Values	
		Expected %	Obtained %
C	2.0 to 4.0	90	88
Mn	0.3 to 1.5	95	95
P	.05 to 0.8	100	99
S	.03 to .2	80	68
Si	.5 to 3.2	95	90
Cu	.2 to 1.5	100	101
Ni	.1 to 3.0	100	100
Cr	.08 to 2.0	100	100
V	.02 to 0.25	100	103
Mo	.15 to 1.5	100	100

a small error in the assignment of the vanadium content in the ferrovanadium used.

7. PRELIMINARY ANALYSIS

Prior to pouring the molten metal into the mold, two ladle samples to serve for preliminary analysis were obtained by casting into separate containers mounted on the copper plate. These samples were designed to be similar to the cast standard samples in size and shape. One of these samples was fractured and examined rapidly before casting the main heat to determine whether the white iron structure was obtained throughout the casting thickness. Had the test sample for any of the heats exhibited evidence of free rather than

combined carbon, a further addition of tellurium to the molten metal in the ladle was planned.

The sample which had been fractured was retained at NBS for preliminary analysis; the second sample was sent to a cooperator* for preliminary analysis and for application evaluation by comparison with their analyzed spectrochemical cast iron samples.

With the exceptions of carbon, phosphorus, and sulfur, which were determined chemically, spectrochemical analysis by both optical emission and x-ray served for all other determinations.

Complete analysis for each heat was obtained before preparing a subsequent heat to adjust the recovery values and to ensure adequate coverage of the required concentration ranges for the added elements.

8. HOMOGENEITY TESTING

A large amount of homogeneity testing was deemed necessary because of the new casting procedure and because of the complexity of metallurgical structure in the white iron samples. At NBS, this testing was accomplished primarily by x-ray spectrochemical analysis**; however, optical emission and chemical methods of analysis also were employed, as well as metallographic examinations. In addition, four cooperating laboratories provided major contributions toward the

* W. R. Kennedy, American Cast Iron Pipe Co., Birmingham, Ala.

** Spectrochemical Analysis Section, National Bureau of Standards, Washington, D. C. (D. M. Bouchette, Jr.)

homogeneity testing* .

For each standard, several samples were chosen to test for variations in composition and structure: (1) from bottom to top and from inside to outside of the individual samples; (2) among samples from different locations in the same grid mold; and (3) among samples from each of the nine grid molds. As a result of detailed metallographic studies and in combination with homogeneity testing of composition, it was determined that the full sample thickness of 3/4 in. was not sufficiently uniform and the decision was made to certify only the bottom half of the samples. When this was done, the variations in structure and composition were found to be within limits adopted for certification.

In the metallographic examination, samples from each of the eight prepared white irons showed near the chill cast surface a columnar type of structure which extended upward approximately one-half the sample thickness; above this the structure consisted of randomly oriented dendrites. The change to random orientation was gradual in samples of NBS Nos. 1178 and 1180, with no distinct boundary between the two types of structures as was true for the other white irons.

*

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General Motors Corporation, Research Laboratories,
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International Harvester Co., Manufacturing Research,
Chicago, Ill. (M. E. McKinney).

Table 5 shows some typical x-ray results of homogeneity testing for manganese, nickel and molybdenum in the brake drum standard, NBS No. 1179. Similar test data were obtained for each of the 20 elements contained in the eight white iron standards.

To make the standards available for issue at the earliest possible date, it was planned to provide initial certification for only the first 10 elements shown in table 1. Following evaluation of the homogeneity test data, the 10 elements were found to have acceptable homogeneity in all eight standards.

In several instances, the results of the statistical evaluation (table 5) indicated definite inhomogeneity; the amount, however, was small and was deemed acceptable from the practical standpoint. The criterion adopted for statistical significance of inhomogeneity was that the total difference between the two main items for contrast must exceed three times the test level. The test level is the standard deviation of the reported average which is obtained by dividing the calculated standard deviation by the square root of the number of values on which the average is based.

Providing that the analytical method of testing provides high precision, such as shown for the "within plate" testing for molybdenum, and depending on the number of replications, it is frequently possible to observe statistical significance for inhomogeneity. The "within plate" test level for molybdenum is only 0.000₂ percent; thus a difference between

Table 5. Typical Homogeneity Test Data: Manganese, Nickel, and Molybdenum in Brake Drum Standard, NBS No. 1179, by X-Ray Determinations.

Test	Manganese	Nickel	Molybdenum
<u>Within Sample</u>			
Bottom, % (Av. of 4)	0.6423	1.349	0.3259
Center, % (Av. of 4)	.6437	1.351	.3261
Difference, %	.0014	0.002	.0002
Difference from mean, %	.0007	.001	.0001
% Difference from mean	.11	.07	.03
*Test level, %	.0018	.002	.0014
Significance			
Statistical	no	no	no
Practical	no	no	no
<u>Within Plate</u>			
Center, % (Av. of 8)	0.6458	1.338	0.3277
Edge, % (Av. of 8)	.6402	1.362	.3243
Difference, %	.0056	0.024	.0034
Difference from mean, %	.0028	.012	.0017
% Difference from mean	.44	.89	.52
Test level, %	.0030	.002	.0002
Significance			
Statistical	no	yes	yes
Practical	no	no	no
<u>Among Nine Plates</u>			
Maximum, % (Av. of 4)	0.6533	1.359	0.3277
Minimum, % (Av. of 4)	.6363	1.343	.3248
Difference, %	.0170	0.016	.0029
Difference from mean, %	.0085	.008	.0014
% Difference from mean	1.32	.59	.43
Test level, %	.0042	.001	.0004
Significance			
Statistical	yes	yes	yes
Practical	no	no	no

*

Test level: standard deviation of the reported average.

"center" and "edge" as small as 0.0006 percent would appear statistically significant. At the concentration level of about 0.3 percent for molybdenum, such a small difference has little practicality. If it is assumed that certification will be to the nearest 0.01 percent, the actual difference found of 0.003₄ percent (\pm 0.001₉ percent from the mean) also has no practical significance. Practical significance is adjudged on the basis of (1) method precision, (2) number of replications in testing, (3) the concentration of the element under test, and (4) the accuracy of the certification (which may itself, in some instances, be limited by the homogeneity). For the concentration range of about 0.1 to 5 percent, a variation of approximately of \pm 1 percent of the amount present is normally acceptable, whether or not statistical significance is observed. The value of \pm 1.3 percent for manganese among the nine plates was deemed acceptable from the practical standpoint although falling somewhat outside of the \pm 1 percent criterion.

9. SAMPLE IDENTIFICATION

Since only half of the sample was found of suitable homogeneity, it was important that positive identification of the certified portion be made known. Figure 2 shows a schematic diagram of the NBS white cast iron spectrometric samples. As can be seen, the samples have been numbered on the face opposite to the chill cast surface.

SCHEMATIC DIAGRAM OF NBS WHITE CAST IRON SPECTROMETRIC SAMPLES

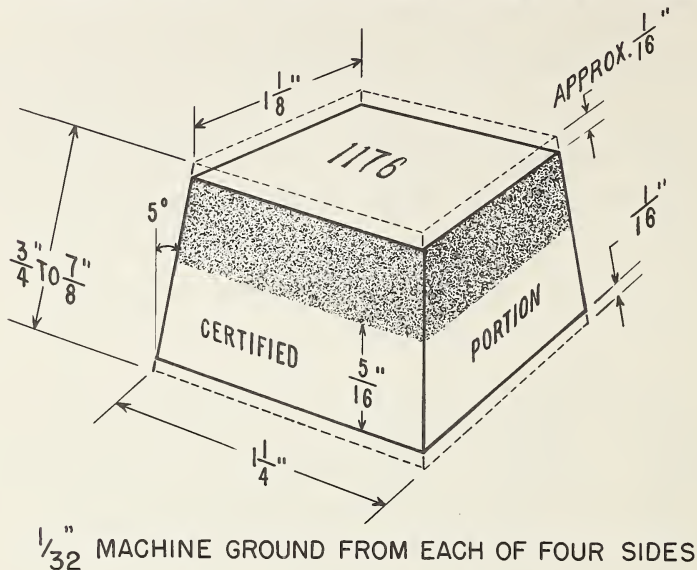


Figure 2. Schematic diagram of NBS white cast iron spectrometric samples.

The samples were cast with a taper to the sides. This offers positive and permanent identification of the certified portion of each sample by noting that the test face always will be the largest surface. The exact certified portion is that extending upward $\frac{5}{16}$ in. from the test surface of the sample as received. Only this portion was analyzed in the cooperative program for certification.

Because of the extreme hardness of the white cast irons, it was necessary to number the samples by abrasion with

carborundum dust blown through a template under high air pressure. Since the indentation is shallow, care will be required in the laboratory to maintain identities. A further complication is the fact that the white iron samples are subject to rather severe rusting.

10. HEAT TREATMENT

The high susceptibility of the cast samples to cracking during the final processing operations posed a serious problem not only for the original sample preparation at NBS, but also to the ultimate user. As a consequence, it was essential to study the stress relief heat treatment of these drastically chilled castings to arrive at a compromise that would permit a reasonable amount of careful grinding and yet not cause enough metallurgical change in the material to initiate graphite precipitation [4].

A series of stress relief heat treatments over the temperature range of 370 to 815°C (700 to 1500°F) for one hour were given to samples from each of the eight standards. By metallographic examination, the presence of a graphite or carbon precipitate could not, in some instances, be definitely determined; however, graphite was definitely present in most samples having received the 815°C (1500°F) treatment. None of the specimens treated at 595°C (1100°F) showed graphite precipitation. Moreover, samples treated at this temperature were found to be free from cracking during sectioning, grinding, or polishing. As the result of these tests, all samples were

given the selected heat treatment of one hour at 595°C. It is important to note, however, that the samples are still sensitive to cracking by careless cutting or grinding.

11. CHEMICAL ANALYSIS

Samples for cooperative chemical analysis for certification were obtained by breaking brittle segments, cut from the certified portion of representative samples, in an iron mortar with an iron pestle. Chemical analyses were made at NBS and in five cooperating laboratories*. Provisional Certificates of Analyses were prepared in April, 1961 and the samples released for issue; the values appearing on the Certificate for the 10 elements in the eight standards are shown in table 6**. By comparing these values with those for the planned compositions (table 1), it is clear that close

*

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A brief summary of the chemical methods used to determine each of the 10 elements, together with a listing of the cooperative results, is available on request to the Analytical Chemistry Division, National Bureau of Standards, Washington, D. C.

Table 6. Provisional Certified Values for Eight NBS
White Cast Iron Spectrochemical Standards
(April 1961)

NBS No. Designation Element	1176	1177	1178	1179	1180	1181	1182	1183
	Piston Ring	Wear Plate	Die	Brake Drum	Mold	Modified		
	%	%	%	%	%	A	B	C
C	3.47	2.74	3.11	3.35	3.28 ^a	3.63	1.97	3.05
Mn	0.63	0.37	0.86	0.64	1.12	1.32	0.45	0.91
P	.42	.61	.115	.23	0.055	0.29	.85	.011
S	.061	.037	.026	.165	.086	.052	.046	.025
Si	3.19	.88	1.91	1.35	3.04	2.54	.31	1.76
Cu	0.76	.087	0.16	0.41	0.20	1.47	.49	1.01
Ni	.055	2.97	2.25	1.31	.044	0.11	.22	0.53
Cr	.51	1.39	0.89	0.23	.14	2.04	.029	.077
V	.17	0.005	.017	.036	.26	0.11	.060	.080
Mo	.59	1.49	.94	.31	.155	.042	.018	.029

a

This standard contains some free graphite (approximately 0.1 percent; the other standards contain less than 0.01 percent).

agreement for most was obtained.

Current plans are to certify additional elements in these standards as well as in new cast iron standards.

12. CONSISTENCY TESTING

Following completion of the analytical program for certification, but prior to issue of the standards, a consistency test was performed. In this test, applications of the standards in both optical emission and x-ray methods

were investigated. The standards should provide points which fit smooth analytical calibration curves when compared as a set and when compared with other reliable standards.

Several sets of individual company standards (not generally available) were provided to NBS on a loan basis. Good agreement was observed among the eight NBS standards and among the sets of standards for the elements manganese, silicon, copper, nickel, chromium, vanadium, and molybdenum. For carbon, a bias was exhibited between different sets when examined with vacuum optical emission spectrometers by outside cooperating laboratories*. It was determined that the degree of chill was critical for the carbon determination. This finding serves to emphasize the important requirement that samples for analysis and standard samples must be closely matched with respect to all variables, such as size, shape, composition, and metallurgical condition. Any departure from this principle must be investigated thoroughly to ensure that a bias has not been introduced.

Whereas the results of the consistency testing demonstrated that the NBS standards can be used directly in the laboratory for the analysis of white iron samples for elements other than carbon, local re-evaluation or the preparation of additional reference samples may be required for the carbon determination by spectrochemical means.

*

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13. PRECAUTIONS FOR APPLICATION

Several precautions need to be taken in the application of these standards to spectrochemical analysis. The surface preparation for x-ray spectrochemical analysis was found to be critical since the samples exhibited metallurgical structure changes not only among the standards, but also from bottom to top of the certified portion of each sample. It is known, for example, that careful surface preparation normally is required for the determination of the light elements, those below atomic number 22. This is because nearly all of the emitted secondary radiation from the sample is absorbed except for that emanating from the immediate surface. A metallographic polishing technique has proven to be the ultimate in surface preparation for solid metallic samples [5]. This minimizes the effects of differences in structure as affected by surface preparation, and the effects of tearing or smearing of the surface of samples for analysis. For application of the standards to x-ray analysis, each laboratory will need to ascertain the surface preparation necessary to minimize apparent differences in composition not only among the standards, but also between standards and samples for analysis as well.

Although the change in structure may influence the results of optical emission analysis, depending on the excitation and exposure conditions, this generally was not

found to be a serious problem. Apparent differences in composition were observed in optical emission analysis, however, from center to outside of a sample rather than from bottom to top as was exhibited by x-ray. To confirm this finding, the x-ray beam was masked to provide an irradiated area on the sample about the same size as the optical emission burn. The same testing was performed, but no significant differences in composition were observed. On further investigation, the apparent differences exhibited by optical emission were attributed to a differential heating effect.

The heat conductivity of the white iron samples was found to be poor. In effect, just the sparked surface and the immediate adjacent area became hot, not the entire sample as was true for copper or steel. Thus differences in volatility rates for some elements occurred with the white iron samples and these were dependent on the location of the area sparked. Near the edge of the sample the heat was dissipated more rapidly to the atmosphere in contrast to center positions where the heat dissipation was restricted largely by the poor conductivity of the metal. To obtain the most reliable optical emission results, then, each laboratory should closely match standards and samples for analysis not only with respect to size and shape, but also with respect to the position of sparking.

Although not believed to be critical in application, it should be noted that NBS Standard No. 1180 was found to contain approximately 0.1 percent of free graphite; the other standards all were found to contain less than 0.01 percent.

14. ADDENDUM

Two new white cast iron standards, a high- and a low-composition alloy, were melted and cast in February, 1964. These standards were required in view of the limited supply of eight standards prepared previously and they are designed to serve the long-term need for this type of standard. Homogeneity testing is now underway and if satisfactory the standards will be certified initially for Ti, As, Sb, Sn, Co, Te, B, Bi, Pb, Zr, and Al.

The two new white cast iron standards were also prepared at the Naval Research Laboratory, using procedures similar to those described previously except that a double quantity was melted and two gang castings were made for each heat. Non-volatile elements were added to the initial melt, one half of which was then tapped into a ladle and poured into a holding furnace. The volatile elements were added to the melt in the original furnace and the first gang casting completed on the water-cooled copper plate. After preparing a second mold assembly, which required less than one-half hour, the holding furnace was brought to temperature, identical quantities of the volatile elements added, and the second gang casting completed.

Since small differences in composition will undoubtedly exist between the first and second gang casting for each standard, the second casting in each case will be treated as a separate standard. It will be issued as a renewal standard when the quantity of the first casting has been exhausted, although it will be tested and analyzed simultaneously with the first casting.

A narrated, color, motion picture showing the melting and casting of the new NBS white cast iron standards is being prepared under the direction of the Naval Research Laboratory personnel. The National Bureau of Standards will have a copy available for loan by fall of 1964.

15. References

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