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Standard Reference Materials:

**PREPARATION OF NBS
COPPER-BASE SPECTROCHEMICAL
STANDARDS**



**U.S. Department of Commerce
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** Located at Boulder, Colorado.

Standard Reference Materials:

**Preparation of NBS
Copper-Base Spectrochemical
Standards**

Robert E. Michaelis, LeRoy L. Wyman, and Richard Flitsch

**Institute for Materials Research
National Bureau of Standards
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 260-1, Preparation of NBS White Cast Iron Spectrochemical Standards, June 1964. 30 cents.

NBS Miscellaneous Publication 241, Standard Materials Issued by the National Bureau of Standards: A Descriptive List with Prices, March 1962. 30 cents. Up-to-date supplementary insert sheets to Misc. Publ. 241 list new, renewal, out of stock, and discontinued standards. This sheet is available without charge directly from the National Bureau of Standards, Washington, D.C., 20234.

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

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PREPARATION OF NBS COPPER-BASE SPECTROCHEMICAL STANDARDS

Robert E. Michaelis, LeRoy L. Wyman, and Richard Flitsch

Institute for Materials Research, National Bureau
of Standards, Washington, D.C.

A procedure has been developed for the preparation of copper alloys in both the chill-cast and wrought forms, sufficiently uniform in composition and microstructure for calibration and use as standard samples in spectrochemical analysis. The method involves casting the molten metal on a massive water-cooled copper plate producing unidirectional cooling. A large disk casting 27 in. in diameter and about 4 in. high is obtained which is split laterally into two pieces, the lower section providing standards in the chill-cast condition and the upper section material for subsequent fabrication into standards for the wrought condition. Details of the planning, preparation and testing of the standards material for 21 compositions are given, and application of the samples in calibration for optical and x-ray spectrochemical analysis is described.

1. INTRODUCTION

Spectrochemical analysis of alloys usually is complicated by the fact that the component elements react to form intermediate phases, and these constituents represent different energy relationships from each other. As a consequence, it requires different amounts of energy input to excite a given component atom, depending on how tightly it is bonded to itself or to other components in the various constituents of an alloy system. Because of this, the uniformity of the microstructures of samples for spectrochemical standards is vitally important. Particularly is this true for the copper-base alloys such as the brasses and the bronzes.

The need for copper-base spectrochemical standards has existed for a considerable length of time. For example, a survey made in 1950 by ASTM Committee E-2 revealed that standards were required to cover more than 50 different types of copper-base alloys. Of greater significance than numbers of standards, however, was the realization that the effects of disperse phases and physical characteristics on the spectral excitation seriously complicated the spectroscopic analysis for many of the copper alloys. To illustrate, it was known that as the copper-rich end of an alloy system was approached, a small change in composition could markedly affect the electrical properties and heat conductivity, and hence the volatility rates in spectral excitation. It was no wonder, then, that chill-cast versus wrought samples frequently led to major differences in the spectrochemical results. Moreover, differences often were observed depending on the size, shape, and material of the molds used in obtaining chill-cast samples, the type of heat treatment for wrought samples, and the surface preparation of both types of samples for spectrochemical analysis.

In 1955, a cooperative program was initiated between the NBS and a Task Group of Subcommittee V, ASTM Committee E-2, to plan for the preparation of a limited number of needed copper-base standards.

The main purposes of this paper are to describe the development of a satisfactory method for the preparation of

the copper-base standards and to evaluate the application of this method to 21 prepared copper-base compositions for NBS spectrochemical standards.

2. PRELIMINARY PLANNING

As a result of several initial meetings with the ASTM Task Group, three main recommendations were adopted. (1) Standard samples were to be prepared for seven principal copper-base alloys: cartridge, free-cutting, naval, red, and aluminum brasses, gilding metal, and commercial bronze. Close liaison was maintained with the Copper and Copper Alloy Spectrographic Committee of the Canadian Association for Applied Spectroscopy to prevent duplication of efforts since this group also was planning the preparation of standards. (2) Three standards were to be provided for each alloy consisting of a nominal, a high, and a low composition. Thus, individual analytical curves could be established to eliminate the effects of matrix composition for the seven alloys; but equally significant, standards would be available for study of these effects for application to other copper-base alloys. (3) Finally, it was considered important to prepare both chill-cast samples primarily for the producer and wrought samples primarily for the consumer for each composition. By so doing, the problems attributed to chill-cast versus wrought samples or standards would not exist.

3. CONSIDERATION FOR PREPARATION

At the same time as consideration was being given at NBS to the preparation of the copper-base standards, studies were also being devoted to the preparation of a set of eight white cast iron spectrochemical standards [1]. For both, it was noted that the preparation of spectrochemical standard samples to be provided in the "as cast" condition presented several difficulties not encountered in those which could be provided in the wrought condition. Further complicating the preparation of the copper-base standards was the necessity of providing both chill-cast and wrought samples.

Since it is next to impossible to obtain complete homogeneity from conventional castings or ingots of any size from melts having complex compositions, it was evident that advantage must be taken of the generally accepted method to minimize segregation, namely, to solidify the molten metal as rapidly as possible. For the cast iron standards, it was believed that a scheme of rapid unidirectional solidification from the melt would provide samples of suitable homogeneity which would be useful both in optical emission and in x-ray spectrochemical analysis. Although differing in details from the cast iron, another scheme utilizing rapid unidirectional solidification was considered for the preparation of the copper-base material by which, and on further processing, it was believed that both chill-cast and wrought samples could be obtained from the same casting.

The main advantage of rapid unidirectional solidification over other types for the preparation of spectrochemical standards is not that it eliminates segregation, but that it does force the segregation to occur largely at the top of the casting where it may either be removed or where it at least does not interfere with optical emission or x-ray spectrochemical analysis.

4. CHEMICAL COMPOSITIONS

As indicated previously [1], modern metallurgy is concerned not only with those elements that may be considered the main components of an alloy, but also with the effects of minute amounts of other elements. For the copper-base standards, it was deemed essential to provide suitable standards containing all of the trace elements of interest; however, it was not believed necessary to provide a graded and certified series for each of the seven alloys.

In 1955 the NBS, in cooperation with the copper industry, planned the chemical compositions for three standards each of seven copper-base alloys. The final compositions adopted by NBS and accepted by industry are shown in table 1. As can be seen, each alloy is covered by a nominal, high, and low composition standard. All of the elements covered by the then present and proposed chemical specifications were included for each alloy type; additionally, all of the trace elements of interest were purposely included only in the cartridge brass series.

Table 1. Planned Compositions of NBS Copper-Base Spectrochemical Standards

Designation	Code	Cu	Pb	Fe	Zn	Other and Remarks			
Cartridge Brass	Spec.	68.5-71.5	0.07 max. ^a	0.05 max. ^b	Remainder	Total Others 0.15 max.			
	A1	67.0	0.10	0.10	(32.58)	*(see below)			
	A2	70.0	0.05	0.04	(29.84)	*(see below)			
	A3	73.0	0.02	0.01	(26.94)	*(see below)			
Free-Cutting Brass	Spec.	60.0-63.0	2.5-3.7	0.15 ^c	Remainder	Other 0.50 max.			
						Sn	Ni		
	B1	59.0	4.0	0.30	(35.75)	0.80	0.15		
	B2	61.5	3.0	0.10	(34.95)	0.40	0.07		
Naval Brass									
	B3	64.0	2.0	0.05	(33.72)	0.2	0.03		
	Spec.	59.0-62.0 ^d	0.20 max.	0.10 max.	Remainder	Sn 0.5-1.0 Total Other 0.10 max.			
						Ni	Al	Mn	
Red Brass (85-15)									
	C1	58.7	0.03	0.02	(40.40)	0.75	0.06	0.02	0.02
	C2	61.0	0.15	0.07	(37.40)	1.2	0.10	0.08	--
	C3	65.0	0.06	0.08	(34.37)	0.42	0.03	0.03	0.01
Gilding Metal (95-5)	Spec.	84.0-86.0	0.06 max.	0.05 max.	Remainder	Total Other 0.15 max.			
						Sn	Ni		
	D1	82.0	0.07	0.07	(17.66)	0.10	0.10		
	D2	84.5	0.03	0.03	(15.34)	0.05	0.05		
Commercial Bronze (90-10)									
	D3	87.0	0.01	0.01	(12.94)	0.02	0.02		
	Spec.	94.0-96.0	0.05 max.	0.05 max.	Remainder	Total Other 0.13 max.			
						Sn	Ni		
Aluminum Brass									
	E1	93.5	0.07	0.07	(6.16)	0.10	0.10		
	E2	95.0	0.03	0.03	(4.84)	0.05	0.05		
	E3	96.5	0.01	0.01	(3.44)	0.02	0.02		
Commercial Bronze (90-10)	Spec.	89.0-91.0	0.05 max.	0.05 max.	Remainder	Total Other 0.13 max.			
						Sn	Ni		
	F1	88.0	0.01	0.07	(11.72)	0.10	0.10		
	F2	90.5	0.03	0.03	(9.34)	0.05	0.05		
Aluminum Brass									
	F3	93.0	0.07	0.01	(6.88)	0.02	0.02		
	Spec.	76.0-79.0	0.07 max.	0.06 max.	Remainder	Al 1.8-2.5 As, Sb, or P 0.02-0.10			
						Al	As	Sb	P
Aluminum Brass									
	G1	75.0	0.02	0.07	(21.97)	2.8	0.01	0.01	0.12
	G2	77.5	0.05	0.03	(20.14)	2.1	0.06	0.06	0.06
	G3	80.0	0.10	0.10	(18.14)	1.5	0.12	0.12	0.01

*Total Other Impurities 0.15 Max.

	Spec.	Sn	Ni	Sb	As	Mn	Si	Bi	Te	Al	Be	P	Cd	Ag
Cartridge Brass	A1	0.05	0.05	0.02	0.02	0.02	0.01	0.0008	0.005	0.008	0.002	0.008	0.015	0.020
(Continued)	A2	0.015	0.015	0.01	0.01	0.01	0.005	0.0001	0.002	0.003	0.001	0.003	0.003	0.009
	A3	0.005	0.005	0.005	0.005	0.0035	0.002	0.0003	0.001	0.0003	0.00015	0.001	0.005	0.004

- ^a Pb may be 0.30 max. for some specifications.
^b Fe may be 0.10 max. for some specifications.
^c Fe allowed to 0.35 max. for one specification.
^d Cu allowed to 65% for some specifications.

5. CASTING

The massive water-cooled copper-mold assembly that was designed and constructed at NBS for the unidirectional casting of the copper-base alloy standards. This mold assembly has been described in detail elsewhere [1], but essentially it consists of a plate, 64 in. sq. by 1 in. thick, made of OFHC copper (oxygen free-high conductivity) and which is water cooled on the bottom side.

To accomplish the casting of the copper-base alloys, it was reasoned that if a sufficiently thick disk could be cast and solidified in but a few minutes, then a minimum of heterogeneity would result. Moreover, the chill-cast face of the disk could serve to provide the as-cast samples, while a portion of the remaining thickness of the disk could be fabricated into bar stock 1 1/4 in. in diameter and sliced to form the wrought samples.

The thickness of the disk would need to be about 3 1/2 or 4 in. to allow for (1) a smoothing cut on the chill-cast face, (2) parting cuts, (3) finished sample thickness of 3/4 in. for the as-cast samples from the bottom layer and (4) adequate thickness of the top layer both to permit rejection of the objectionable top surface of the casting and to provide sufficient material for working into round bars 1 1/4 in. in diameter.

With the thickness of the casting limited by the above requirements, the diameter of the disk would be established

by the number of samples desired. Inasmuch as this might vary, it was decided to define the periphery of the disk by means of iron castings, slightly arched, and having a tongue at one end and a groove at the other to permit interlocking; the size of the annulus being defined by the number of blocks in the circle. A disk size of 27 in. in diameter finally was adopted.

To minimize the peripheral chilling of the casting by the iron blocks and thus to obtain the maximum unidirectional chill from the plate, an inner wall, 3 in. thick, of baked-sand forms was assembled within the cast iron ring, and their joints sealed.

In pouring the casting, several schemes were investigated which included lip-and bottom-pouring from ladles, and rapid dumping of the melt. The criterion here was to permit complete coverage of the disk area in the minimum of time but with neither cold shuts nor splatters. This study resulted in the adoption of a tun dish (pouring basin) having six stoppered orifices into which the entire melt was poured, and from which all metal was run onto the casting plate by simultaneously releasing the six stoppers.

6. MELTING

Following extensive investigations in the NBS foundry during 1957 and 1958, which included the preparation of one cartridge brass and one naval brass standard, techniques of melting, casting, and fabrication were established for

producing suitable chill-cast and wrought samples from a single casting.

Experimental melting at NBS was carried out in a high-frequency induction furnace of 1,000-lb rated capacity; however, all production heats with the exception of the one cartridge and one naval brass were made at the Naval Research Laboratory* in a similar type of furnace also of 1,000-lb rated capacity.

High-purity metals were used either directly or in the preparation of master alloys, and these are shown in table 2. The copper was OFHC grade; the zinc was five nines pure and added as a prepared and analyzed 50 copper-50 zinc alloy.

Heats of approximately 600 lb were melted under a charcoal cover. 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 a cartridge brass standard (Code Al in table 1). For this standard it is noted that the iron, nickel, and manganese additions were made with the initial furnace charge. On subsequent melts, these additions were combined, melted separately in a small gas-fired furnace, and added in the molten condition to the main melt at the same

*

The authors express their appreciation to L. DePue and the foundry staff at the Naval Research Laboratory for permitting the use of their facilities and personnel in the production of the 19 remaining copper-base spectrochemical standards.

Table 2. Materials Used in Melting NBS
Copper-Base Standards

Element	Material Description	Purity ^a
		%
Cu	OFHC, rod ends	99.9+
Pb	Metal, shot	99 +
Fe ^b	CuFe, small ingot (50% Fe)	99 +
Zn ^b	CuZn, ingot	99.9+
Sn	Metal, small ingot	99.9
Ni ^b	CuNi, small ingot (50% Ni)	99 +
Sb	Metal, lump	99 +
As	Metal, lump	99 +
Mn ^b	CuMn, small ingot (35% Mn)	99
Si ^b	CuSi, broken ingot (10% Si)	99
Bi	Metal, lump	99.5+
Te ^b	CuTe, lump (45.5% Te)	99 +
Al	Metal, small ingot	99.9
Be ^b	CuBe, broken ingot (13.4% Be)	99 +
P ^b	CuP, lump (10% P)	99 +
Cd ^b	CuCd, broken ingot (50% Cd)	99.9
Ag	Metal, chips	99.9+

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

^b A master alloy was prepared for the addition of this element.

Table 3. Log of Melt for a Cartridge Brass
(600 lb) Standard (NBS No. C1100) November 18, 1959

<u>Charge</u>	:	OFHC Cu (199.6 lb), 50 Cu-50 Zn (399.6 lb), 50 Cu-50 Fe (1.2 lb), 50 Cu-50 Ni (0.6 lb), 65 Cu-35 Mn (0.343 lb), charcoal cover.
<u>Furnace On</u>	:	11:05 A.M.
<u>Melt Down</u>	:	Time 11:38 A.M., Temp. 1800°F
<u>Skim</u>	:	Most of charcoal removed. Time 11:42 A.M.
<u>Additions</u>	:	(All were encased individually in copper foil). Pb (272.2 g), Sn (136.1 g), Sb (54.4 g), As (54.4 g), CuMn (155.6 g), CuSi (272.2 g), Bi (2.18 g), CuTe (29.9 g), Al (21.8 g), CuBe (40.4 g), CuP (155.1 g), CuCd (81.6 g), Ag (54.4 g).
<u>Stir</u>	:	Time 11:47 A.M., Temp. 1875°F.
<u>Tap</u>	:	Stir in ladle. Time 11:51 A.M., Temp. 1950 F.
<u>Skim</u>	:	Time 11:53 A.M.
<u>Mold Water on</u>	:	Time 11:54 A.M.
<u>Pour</u>	:	Time 11:54 A.M., Temp. 1920 F. Poured three test samples into ceramic molds on plate edge; followed by pouring entire melt into stoppered basin.
<u>Basin Plugs Pulled</u>	:	Time: 11:56'20" A.M.
<u>Pouring Basin Empty</u>	:	Time: 11:56'35" A.M.
<u>Casting Solidified</u>	:	Time: 11:58'00" A.M.

time as the other additions. This was done to assure complete melting of these higher melting point additives.

For this cartridge brass standard, it can be seen that a total of 1 min 25 sec time had elapsed from pulling the stoppers in the pouring basin to complete solidification for the 600 lb disk 27 in. in diameter and 4 in. thick. The total time varied from about 40 sec to 2 min for the various melts and was dependent primarily on the alloy, but also to a lesser degree on the particular composition for a given alloy.

Figure 1 shows the tapping of the molten metal from the

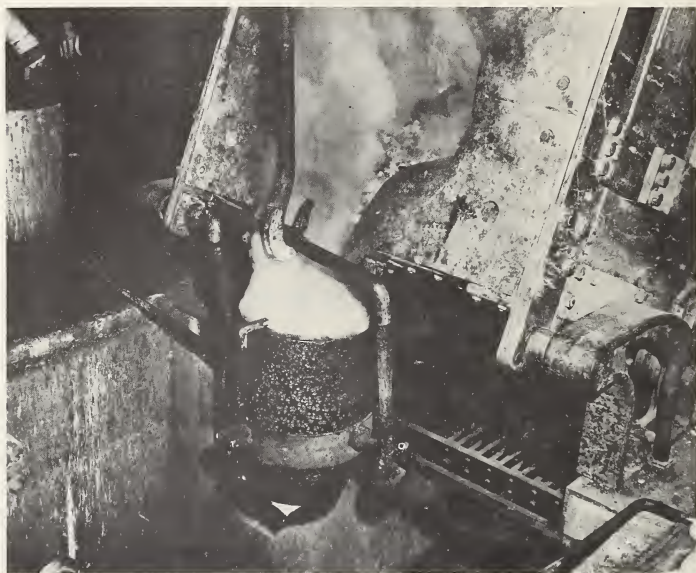


Figure 1. Tapping the molten metal from the furnace into the ladle.

furnace into the ladle. This was done approximately 100°F above the liquidus temperature for each melt. Once in the ladle, the molten metal was skimmed to remove the last of the charcoal cover and the dross.

Figure 2 shows the pouring of test samples into separate ceramic molds on the water-cooled copper plate prior to pouring the main heat. In the background is seen the mold assembly into which the molten metal is poured. Note the stoppered pouring basin at the top. Once the molten metal has been poured into the basin, the plugs are pulled simultaneously.



Figure 2. Pouring of test samples prior to pouring the molten metal into the stoppered pouring basin.

Solidification is unidirectional, from the bottom up, with little freezing occurring from the periphery inward, or from the top downward.

Figure 3 shows a view of the solidified casting. Note the use of the interlocking cast iron blocks to retain the circular disk casting.



Figure 3. Solidified casting on the water-cooled copper plate after removal of pouring basin.

7. PRELIMINARY ANALYSIS

Once a casting had been prepared, preliminary analyses were obtained on the separately cast test samples both at NBS and by a cooperator*. At NBS, both chemical** and spectrochemical determinations were made and a complete analysis for each heat was obtained before preparing a subsequent heat. In general, it was relatively easy to prepare the copper-base castings close to the aim or the desired composition.

8. HOMOGENEITY TESTING

Before processing a casting into standard samples, extensive homogeneity testing was performed and figure 4 shows the selection of samples that were chosen for this testing. Metallographic studies, optical and x-ray analyses, and chemical analyses were made at NBS. In addition, a large amount of testing was performed by members of the cooperating Task Group 3, Subcommittee V of ASTM Committee E-2***. These studies provided information on the composition and structure differences from outside to center and from bottom to top of the casting.

* F. V. Schatz, Revere Copper and Brass, Inc., Rome, N. Y.

** R. K. Bell, Quantitative Separations Section (formerly Standard Reference Materials Section).

*** Task Group 3 cooperators:

Bridgeport Brass Co., Bridgeport, Conn., A. W. Young
Chase Brass and Copper Co., Waterbury, Conn., H. J. Smith
Mueller Brass Co., Port Huron, Mich., S. C. Richards
Olin Mathieson Chemical Corp., New Haven, Conn., R. G. Russell
Revere Copper and Brass, Inc., Rome, N. Y.,
F. V. Schatz (Chairman)

The Anaconda American Brass Co., Waterbury, Conn., J. P. Irwin
Titan Metal Mfg. Co., Bellefonte, Pa., W. M. Rumberger

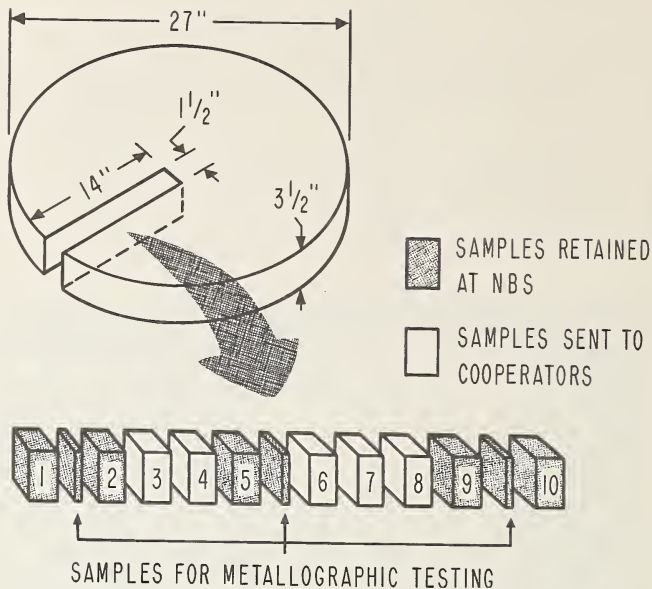


Figure 4. Sampling of disk for homogeneity testing.

Differences in structure were observed by etch tests and metallographic examinations. Figure 5 shows a typical etch pattern through the casting thickness. Extending from the chill-cast surface upward to about half the thickness is the columnar structure indicative of a rapid solidification. Above this are the more randomly oriented large grains of the dendritic structure typical of a slower cooling rate of the molten metal. Finally, near the top, is seen another break in structure where the solidification from the bottom met that coming down from the top. The main purpose of obtaining etch patterns for each casting was to determine that the columnar structure extended upward sufficiently to provide for the



Figure 5. Typical etch pattern of the casting thickness.

chill-cast samples. Although a minimum height of only $7/8$ in. was required, all castings were observed to exhibit this structure to a height of at least $1\ 1/4$ inches. Except for the chill-cast samples, the structure initially was believed to be relatively unimportant, particularly since it would be changed completely during forging. However, on preliminary forging trials considerable radial cracking occurred, and this was attributed to sub-surface porosity that appeared at the interface of solidification from the bottom and top of the casting. Thus, the etch pattern also served to determine the amount of material that had to be removed from the casting top to prevent cracking on subsequent forging.

Although homogeneity studies did demonstrate some non-uniformity of composition near the casting top, the entire

casting thickness generally was found to be considerably better than was anticipated. When the material at the top containing the sub-surface porosity was removed, the remaining material for most castings was found to be of high homogeneity. Typical results of a homogeneity study are shown in figure 6. The test positions on a section of the casting thickness are indicated on the sketch; three such sections from center to outside of the casting were examined. The test level indicated at the bottom 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. In general, differences among positions exceeding the test level values are statistically significant at the 5 percent level. Iron shows no difference from bottom to top at the test level of four parts per million.

Lead shows a statistically significant trend of increasing content from top to bottom but this was deemed to have little practical significance. Position 4 differs from positions 1, 2 and 3 for both nickel and zinc. Even including position 4, the variation for nickel is acceptable. For zinc, however, cutting the top portion to discard does considerably reduce the variation. Practical significance of inhomogeneity 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.

TYPICAL RESULTS OF HOMOGENEITY TESTING

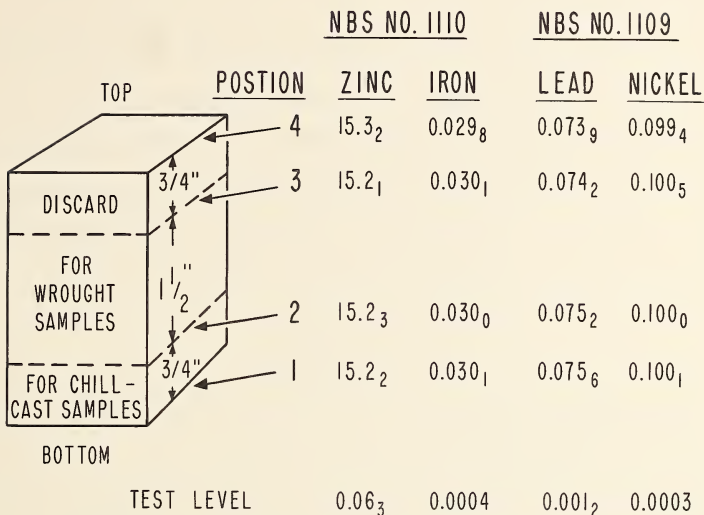


Figure 6. Typical results of homogeneity testing.

An example of the latter situation exists for lead (3% nominal) in free-cutting brass. Here the lead is added to impart high machineability. Since the solubility of lead in brass is nil, the lead appears as small soft particles dispersed throughout the brass matrix. Although not necessarily a factor in the end use of the material, certain variations do occur in the particle size and in the distribution of the lead. With lead, then, the inherent heterogeneity limits the accuracy of the certification. Whereas ± 1 percent of the amount present is normally acceptable from the practical significance standpoint, with lead in free-cutting brass ± 5 percent of the amount present is deemed acceptable, but this in turn, limits the

accuracy of certification by reporting values only to the nearest 0.1 percent.

In general, the homogeneity of the copper-base alloy material was found to be sufficiently good so that a single set of results served for both the chill-cast and the wrought samples. For the nominal composition lot of the cartridge brass, however, a practically significant difference was observed between the chill-cast and wrought material necessitating separate certification.

9. PROCESSING

Following acceptance of the homogeneity of the material, the castings were fabricated to finished chill cast and wrought samples. Essentially, about 1/8 in. was removed from the chill-cast face of the casting, 3/4 in. from the top, and 1/2 in. at the periphery. The remaining slab then was cut into strips, the bottom portion of which was further cut to provide the chill-cast samples; and the top portion of which was forged to rods and annealed for the wrought samples.

In forging, the material was soaked in a furnace at the appropriate temperature and then it was worked thoroughly to provide a uniformly recrystallized structure. The proper annealing temperature was determined by metallographic examination and by hardness measurements of samples annealed at 100°F intervals. Intercomparisons were made for each of the three standards for a particular alloy, and with the other alloys as well, to insure the maximum compatibility of the standards.

Because of extreme difficulties encountered in forging some compositions, wrought standard samples will not be available initially for a few standards. For example, the high impurity level standard of both cartridge brass, NBS No. 1100, and red brass, NBS No. 1109, would not permit forging without severe cracking. Additionally, the low lead composition standard (2% nominal) of the free-cutting brass series, NBS No. 1105, and all three of the aluminum brass series, NBS Nos. 1118-1120, also would not forge.

Although the standards described above would not forge, it was believed that an extrusion process could be utilized to produce the wrought samples. In late 1961, test lots of the red brass, NBS No. 1109, and the free-cutting brass, NBS No. 1105, were sent to Nuclear Metals, Inc. for extrusion by a procedure agreed upon by both NBS and NMI. Subsequent testing of selected extruded samples indicated that the material should be satisfactory for the wrought samples although some cracking and some nonuniformity of metallurgical structure was in evidence.

Based on the above investigation, the remaining material of all the standards that would not forge (with the exception of the one for cartridge brass which broke up completely on forging and could not be extruded) were sent to NMI for extrusion. Some of the pertinent details of the procedure follow:

(a) the NBS copper-base material was cut into convenient size pieces for close packing in copper extrusion cans (about

6-in. diameter); (b) each cut piece was given a light etch (< 5 seconds) in dilute nitric acid before packing in the cans; (c) the cans were evacuated to 0.03 μ pressure at room temperature and sealed; (d) the extrusion temperature was 1550^oF, the ram speed 40 in./min, and the extrusion force from about 700-950 tons; (e) the final extruded size was 1 1/2 in. in diameter.

As with the test lots, some cracking and nonuniformity of metallurgical structure was evident on testing the returned material. Although all the testing has not been completed at this writing, it is believed that the material will be useful as wrought standard samples. A separate report covering the testing of the extruded material has been planned.

10. CHEMICAL ANALYSIS

Samples for cooperative chemical analysis were prepared in the form of millings taken from the cross section of the finished samples of both the chill-cast and wrought material. Chemical analyses were made at NBS for all standards and in six cooperating laboratories, one of which also analyzed all standards.*

* Quantitative Separations Section (formerly Standard Reference Materials Section), National Bureau of Standards, Washington, D.C. (R. K. Bell and E. E. Maczkowske). Analyzed all standards.

Department of Mines and Technical Surveys, Mines Branch, Ottawa, Ontario, Canada (A. E. LaRoche, Elsie M. Penner, C. H. McMaster, and W. R. Inman). Analyzed all standards.

Provisional Certificates of Analyses were prepared for naval brass in March, 1961 (revised in August 1962); for cartridge and red brass in August 1962; and for free-cutting brass, gilding metal, commercial bronze, and aluminum brass in February, 1964. The certified values are shown in table 4**. It is to be noted that additional elements having useful concentration ranges are contained in the cartridge brass series to include Al, Sb, As, Be, Bi, Cd, Ag, and Te.

*(Footnote con't from preceding page)

Anaconda American Brass Co., Waterbury, Conn. (O. P. Case and Mrs. Kathleen M. O'Brien). Analyzed cartridge, naval, and red brass.

Anaconda American Brass Co., Metallurgical Dept., Research and Technical Center, Waterbury, Conn. (Joseph P. Irwin). Analyzed commercial bronze and aluminum brass.

Revere Copper and Brass, Inc., Rome, N.Y., (Frederick V. Schatz and R. E. Hahn). Analyzed free-cutting brass, gilding metal, commercial bronze and aluminum brass.

Mueller Brass Co., Port Huron, Mich. (S. C. Richards, Ray Stevens and Albert Stuever). Analyzed cartridge, naval, and red brass.

Twin City Testing and Engineering Laboratory, Inc., St. Paul, Minn. (Albert C. Holler). Analyzed free-cutting brass.

Ledoux and Co., Teaneck, N. J. (Silve Kallmann). Analyzed gilding metal.

**
A brief summary of the chemical methods used in the analysis of the copper-base alloys is available on request to the Analytical Chemistry Division, National Bureau of Standards, Washington, D.C.

Additionally, a paper is being prepared describing the factors involved in the basic standardization of the x-ray spectrochemical method as applied to the certification of the copper-base alloys. This paper will appear shortly in this publication series.

Table 4. Provisional Certified Values for NBS
Copper-Base Spectrochemical Standards
(May 1964)

Cartridge Brass				
NBS No. ^a	b C1100	1101 c	c C1101	1102 C1102
Element ^d	Percent			
Cu	67.4 ₃	69.6 ₀	69.5 ₀	72.8 ₅
Zn	32.2 ₀	30.2 ₆	30.3 ₄	27.1 ₀
Pb	0.106	0.05	0.05	0.020
Fe	.072	.037	.037	.011
Sn	.055	.016	.016	.006
Ni	.052	.013	.013	.005
Mn	(.003) ^e	(.006)	(.006)	(.004)
P	(.01)	(.002)	(.002)	(.006)
Si	(.01)	(.005)	(.005)	(.002)

Free-Cutting Brass				
NBS No. ^a	1103 ----	f C1103	1104 C1104	b C1105
Element ^g	Percent			
Cu	59.2 ₇	59.1 ₉	61.3 ₃	63.7 ₂
Zn	35.7	35.7	35.3	34.0
Pb	3.7 ₃	3.8 ₁	2.7 ₆	2.0 ₁
Sn	0.88	0.88	0.43	0.21
Fe	.26	.26	.09 ₀	.04 ₄
Ni	.16	.16	.071	.043
P	.003	.003	.005	.003

Table 4. (Continued)

Naval Brass

NBS No. ^a	1106 C1106	1107 C1107	1108 C1108
Element		Percent	
Cu	59.08	61.2 ₁	64.9 ₅
Zn	40.08	37.3 ₄	34.4 ₂
Pb	0.032	0.18	0.063
Fe	.004	.037	.050
Sn	.74	1.04	.39
Ni	.025	0.098	.033
Al	---h	---	---
Mn	.005	---	.025

Red Brass

NBS No. ^a	b C1109	1110 C1110	1111 C1111
Element		Percent	
Cu	82.2 ₂	84.5 ₉	87.1 ₄
Zn	17.4 ₃	15.2 ₀	12.8 ₁
Pb	0.075	0.033	0.013
Fe	.053	.033	.010
Sn	.10	.051	.019
Ni	.10	.053	.022
P	---	---	---

Gilding Metal

NBS No. ^a	1112 C1112	1113 C1113	1114 C1114
Element ⁱ		Percent	
Cu	93.38	95.0 ₃	96.4 ₅
Zn	6.3 ₀	4.8 ₀	3.4 ₇
Sn	0.12	0.06 ₄	0.02 ₇
Ni	.10 ₀	.057	.021
Fe	.07 ₀	.04 ₃	.01 ₇
Pb	.057	.026	.012
P	.009	.008	.009

Table 4. (Continued)

Commercial Bronze			
NBS No. ^a	1115 C1115	1116 C1116	1117 C1117
Element ^j	Percent		
Cu	87.9 ₆	90.3 ₇	93.0 ₁
Zn	11.7 ₃	9.4 ₄	6.8 ₇
Fe	0.1 ₃	0.04 ₆	0.01 ₄
Sn	.10	.04 ₄	.02 ₁
Ni	.07 ₄	.04 ₈	.02 ₀
Pb	.01 ₃	.04 ₂	.06 ₉
P	.00 ₅	.00 ₈	.00 ₂

Aluminum Brass			
NBS No. ^a	b C1118	b C1119	b C1120
Element ^k	Percent		
Cu	75.0 ₇	77.1 ₂	80.1 ₄
Zn	21.9 ₁	20.5 ₃	18.1 ₀
Al	2.80	2.1 ₄	1.4 ₆
Fe	0.06 ₈	0.03 ₃	0.01 ₅
Pb	.02 ₄	.05 ₁	.10 ₅
P	.12 ₅	.07 ₀	.01 ₈

^a Size and metallurgical conditions: 1100 series are wrought samples 1 1/4 in. in diameter, 3/4 in. thick. C1100 series are chill-cast samples 1 1/4 in. square, 3/4 in. thick.

^b The wrought material for this standard is not available.

^c Small differences in the copper and zinc contents made necessary the separate analysis of the wrought and chill-cast material for this standard.

^d Other purposely added elements having useful concentration ranges in the cartridge brass standards include: aluminum, antimony, arsenic, beryllium, bismuth, cadmium, silver, and tellurium. Some of these are expected to be certified at a later date.

- e Values in parentheses are not certified, but are given for information on the composition.
- f Small differences in the copper and lead contents made necessary the separate analysis of the wrought and chill-cast material for this standard.
- g Bi and Ag also are present in small quantities in the standards, but these elements have not been certified.
- h Dashes indicate elements present but not certified.
- i Al, Mn, Ag, and Si also are present in small quantities in the standards, but these elements have not been certified.
- j Ag, Si, and Mn also are present in small quantities in the standards, but these elements have not been certified.
- k Ag, As, Sb, and Si also are present in small quantities in the standards, but these elements have not been certified.

Work currently is underway to certify these elements; also, to provide final certificates for all the copper-base standards wherein the cooperative results will be listed. Completion of the work on the copper-base standards is planned for the fall of this year.

11. PRECAUTIONS FOR APPLICATION

Several precautions are important in the application of these standards to spectrochemical analysis. For the chill-cast samples, the NBS number has been stamped on the surface opposite the chill-cast face. For use in calibration by either optical emission or x-ray techniques, analyses always should be made on the chill-cast surface (opposite that which is numbered).

The determination of lead in the free-cutting brass series by x-ray spectrochemical techniques presents the same problem as lead in leaded steel and is highly dependent on proper surface preparation because of the tendency toward smearing or removal of the lead [2]. It may be found necessary to utilize a metallographic polishing technique to minimize the effects of changes in particle size of an undissolved constituent or in the metallurgical structure size [3].

For use by optical emission techniques, the NBS chill-cast samples are designed for the analysis of samples prepared in a similar manner. It should be cautioned that samples for analysis prepared by casting techniques other than that

of unidirectional solification may produce a bias in the spectrochemical results, the magnitude of which will depend on the excitation parameters.

For wrought material, care should be taken to insure that spectrochemical results obtained on samples relative to the NBS wrought standards are not biased because of differing fabrication techniques or heat treatment.

When the copper content of an alloy is high, 90 percent or more, the heat conductivity, and hence the volatility rate in optical emission analysis, is sensitive to relatively small changes in composition, particularly of copper. At the high copper levels, the heat conductivity also is sensitive to the mass of the samples; therefore, it may be found necessary not only to match samples and standards in terms of size and shape, but also with respect to the positioning of the electrical discharge on the samples. These illustrations serve to emphasize the fact that in order to obtain reliable spectrochemical results, it is imperative to match closely in all aspects the standards and the samples for analysis. Any deviation from this axiom should be investigated thoroughly to insure that a bias has not been introduced.

12. EXAMPLES OF ANALYTICAL CURVES

It is felt desirable to show some examples of analytical curves that can be developed by means of the NBS copper-base standards both by x-ray and by optical emission techniques. These will serve to point to some additional problems that may

be encountered in applications. The analytical curves cover only the first three sets of standards originally made available; viz., cartridge, naval, and the red brass series.

Figure 7 shows the analytical curve for zinc by x-ray analysis. As might be expected, no significant differences between chill-cast and wrought samples are evident. Although some workers have indicated a nickel correction is necessary for the x-ray determination of zinc, certainly one is not required here where the nickel concentration of the standards is 0.1 percent or less.

The situation depicted in figure 8 for nickel by x-ray determinations is not uncommon; that is, where it is not possible initially to draw a single analytical curve through all the points. A reason must exist. The problem for nickel was resolved when a linear correction for a zinc interelement effect was made, along with a background correction, as shown in figure 9. A reasonable fit of the analytical points for nickel now is evident. The enhancement of nickel by zinc, two mass number higher in the periodic table, is of course predictable. The exact effect over wide concentration ranges of zinc may not be linear and would be more difficult to calculate. However, when the effect is not large and when relatively limited concentration ranges are involved, a linear correction normally is sufficient.

It will be of interest to compare the analytical curves of the same elements by optical emission analysis. Figure 10

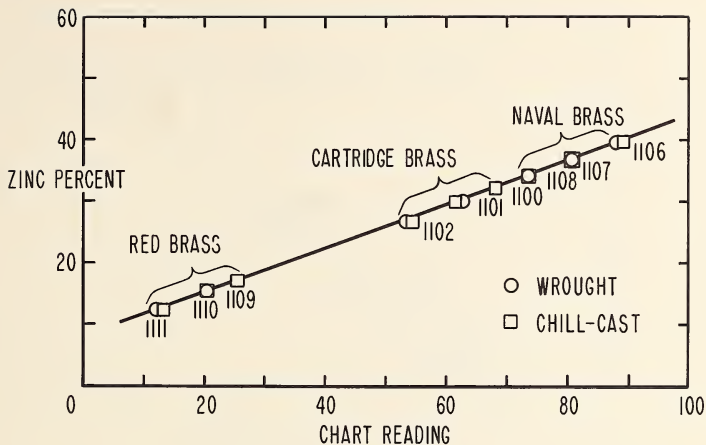


Figure 7. Analytical curve for zinc by x-ray analysis (abscissa is arbitrary units).

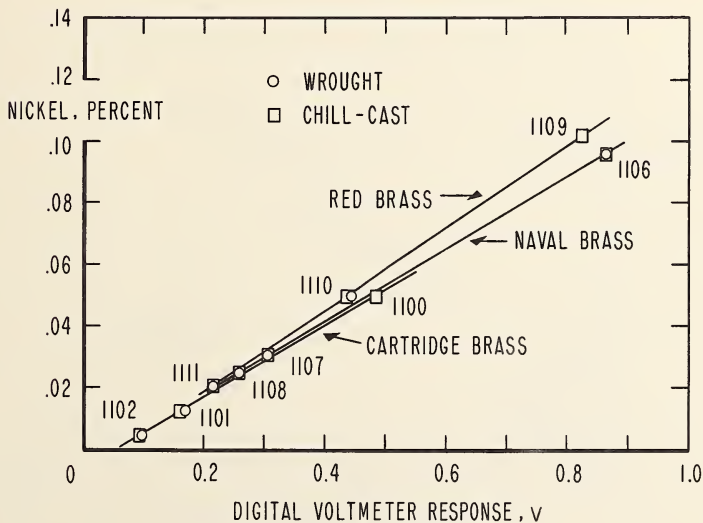


Figure 8. Analytical curve for nickel, by x-ray analysis, uncorrected.

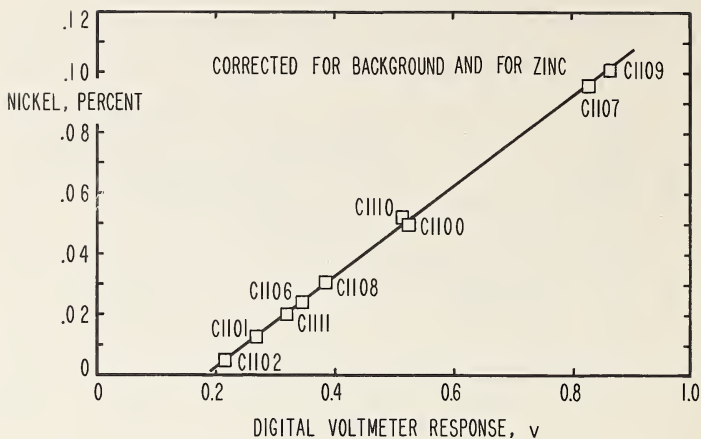


Figure 9. Analytical curve for nickel, by x-ray analysis, corrected for background and zinc.

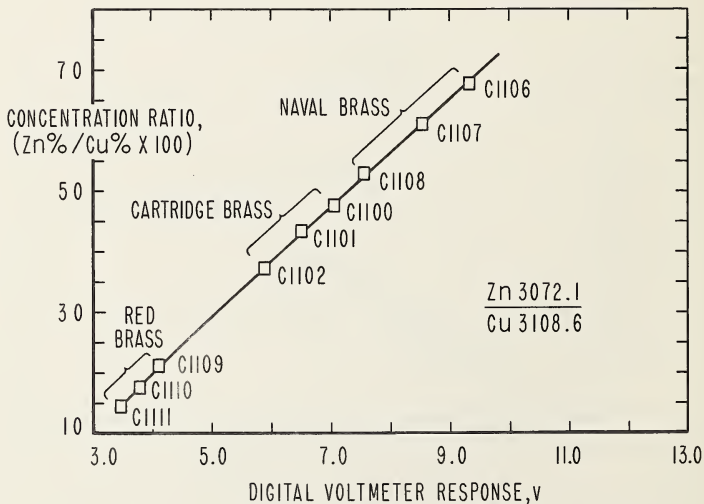


Figure 10. Analytical curve for zinc by optical emission analysis.

illustrates the analytical curve for zinc. Note that by optical emission analysis the ordinate or vertical scale now is in terms of concentration ratio rather than concentration; that is, the zinc content divided by the copper content times 100. This is necessary to correct the intensity of the copper internal standard line for the rather large change in copper content; from about 59 to 87 percent of copper with these standards. Note also that only the chill-cast samples have been plotted. Contrary to expectation, no significant differences have been observed between the chill-cast and the wrought samples for these three alloys. The excitation was provided by a low-voltage triggered spark discharge which was half-wave rectified and adjusted to be critically damped. Other sources or changes in parameters for this source may exhibit differences but these have not yet been investigated. This curve for zinc is perhaps not as good as shown previously by x-ray, but certainly it is acceptable.

Figure 11 shows an analytical curve by an optical emission spectrometer analysis relating the ratio of the Ni 3414.8\AA line in the second order over the Cu 3108.1\AA internal standard line in the first order to the concentration ratio.

Similar to the uncorrected x-ray curve, it is not possible to draw a single analytical curve through all the points. The problem here is not an interelement effect, but an interference that is caused by the third order of the copper line, 2275.2\AA passing through the same slit as the

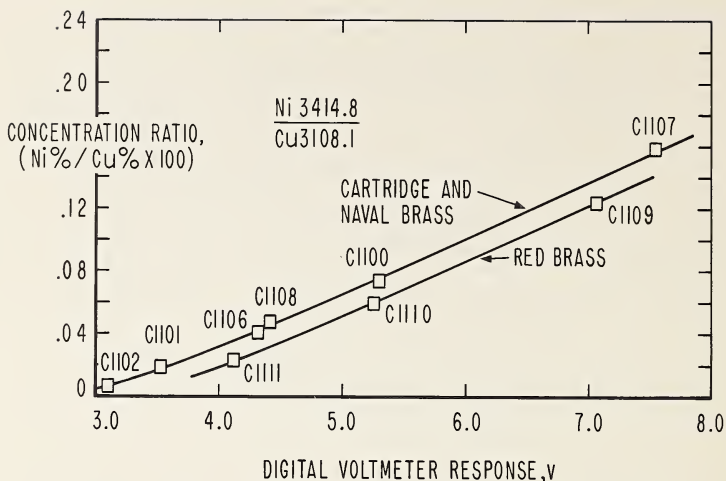


Figure 11. Analytical curve for nickel by optical emission analysis, uncorrected.

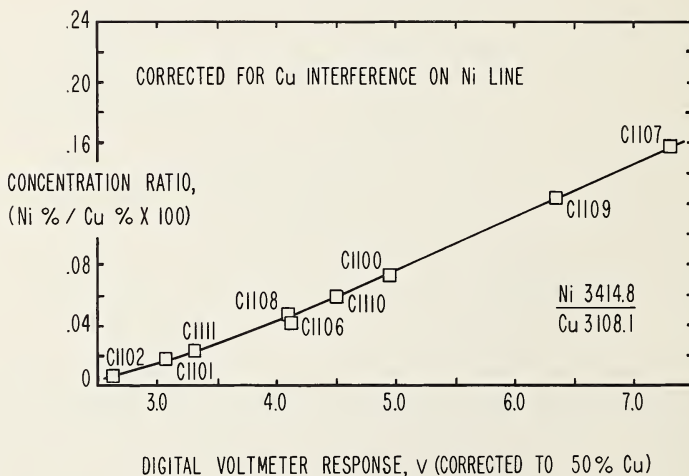


Figure 12. Analytical curve for nickel by optical emission analysis, corrected for copper interference on nickel line.

second order of the Ni 3414.8\AA line. When an appropriate correction is made, a reasonably good curve may be drawn as indicated in figure 12.

A better solution to this particular problem obviously would be to choose another nickel line which would be free from interference. With spectrometers, however, one line of an element may need to serve for several matrices and corrections may be required. In general, good analytical curves for the certified elements were obtained by both x-ray and optical emission analysis.

13. REFERENCES

- [1]. Michaelis, R. E. and Wyman, L. L., NBS Misc. Publ. 260-1, 1964.
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- [3]. Michaelis, R. E., and Kilday, Betty Ann, Advances in X-Ray Analysis, Vol. 5, 405. Edited by W. M. Mueller, Plenum Press, 1962.

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