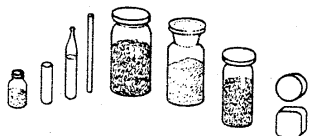
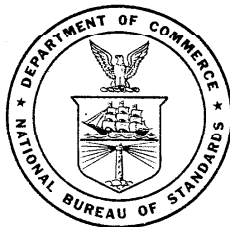


NBS MISC. PUBL. **260-10**



Standard Reference Materials:

**HOMOGENEITY CHARACTERIZATION OF NBS
SPECTROMETRIC STANDARDS II:
CARTRIDGE BRASS AND LOW-ALLOY STEEL**



U.S. Department of Commerce

National Bureau of Standards

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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 representative 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.

W. Wayne Meinke, Chief
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UNITED STATES DEPARTMENT OF COMMERCE • John T. Connor, *Secretary*
NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

Standard Reference Materials:

Homogeneity Characterization of NBS
Spectrometric Standards II:
Cartridge Brass and Low-Alloy Steel

H. Yakowitz, D. L. Vieth, K. F. J. Heinrich,
and R. E. Michaelis

Institute for Materials Research
National Bureau of Standards
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HOMOGENEITY CHARACTERIZATION OF NBS SPECTROMETRIC
STANDARDS II: CARTRIDGE BRASS AND LOW-ALLOY STEEL

H. Yakowitz, D. L. Vieth, K. F. J. Heinrich and
R. E. Michaelis

Institute for Materials Research
National Bureau of Standards

ABSTRACT

Most modern instrumental methods of analysis depend on the use of known standards of composition for calibration. Newer analytical techniques such as the solids mass spectrometer, laser probe and, especially, the electron probe microanalyzer have reduced the amount of a sample which can be analyzed quantitatively to a range of about 0.1 micrograms to as little as 0.00005 micrograms. As a corollary to these microanalytical advances, homogeneity requirements have become severe for the analytical standards. This paper describes a continuation of the NBS effort to more fully characterize existing standards as to suitability for the new microanalytical techniques [1]. An NBS cartridge brass sample in both the wrought (NBS-1102) and chill cast forms (NBS-C1102), as well as an NBS low-alloy steel sample (NBS-463), have been investigated by means of electron probe microanalysis and optical metallography. Some seventeen elements are contained in the brass while twenty-five elements are in the steel. Results for ten elements in the steel are presented while results for six elements in the brass are given. In the steel, Fe, Ni, Cu, and Si are essentially distributed homogeneously at micron levels while Mn, Ta, Nb, Zr, S, and Cr are not. In the brass, Cu and Zn are distributed homogeneously at micron levels while Pb, S, Al, and Si are not. Electron probe microanalyzer results indicate that both NBS-1102 and NBS-C1102 brass are suitable for use as a calibration standard for electron probe microanalysis as well as other microanalytical techniques such as the solids mass spectrometer. The results for brass have been corroborated by a number of laboratories using the electron probe analyzer.

Key words: analytical standards, electron probe microanalyzer, microanalytical techniques, NBS cartridge brass, NBS low-alloy steel, optical metallography

1. INTRODUCTION

The modern day analyst is confronted with many difficult problems in investigating materials to serve our rapidly advancing technology. Increasingly he is asked either (1) to make determinations of chemical elements present in a material at extremely low levels of concentration -- parts per million level and lower; or (2) to provide quantitative analysis of minute sample volumes, a few cubic microns in size. The solids mass spectrometer and the electron probe microanalyzer, respectively, are examples of modern instrumental methods of analysis used by the analyst to aid in solving these analytical problems. The full potential of these powerful analytical tools normally cannot be realized, however, unless they are calibrated by the use of standard reference materials.

Analytical standards serve the analyst in several important ways: (1) calibration of analytical equipment, (2) checking methods of analysis and analytical techniques, (3) developing new or improved methods of analysis, and (4) evaluating the accuracy of analytical techniques. The new microanalytical techniques place severe requirements on the analytical standards particularly with respect to homogeneity.

Although considerable research effort is being devoted to the preparation of analytical standards designed especially for the microchemical techniques, as yet none are available.

The purpose of this report is to describe a continuation of the NBS effort to more fully characterize existing standards

as to their suitability for the new microanalytical techniques [1]. Once characterized, these standards will serve during the interim period until more suitable standards designed especially for microanalytical use can be prepared and certified.

2. MATERIALS INVESTIGATED

In a previous study, low-alloy steel, NBS-461, was fully characterized and found to be sufficiently homogeneous that any present microanalytical technique can be carried out with little chance of inaccuracy due to inhomogeneity [1]. In the light of these encouraging results, it was decided to provide characterization of another low-alloy steel in this series.

On the basis of metallographic examination, it appeared that low-alloy steel, NBS-463, was the best of the remaining seven standards insofar as microstructural homogeneity was concerned. Furthermore, NBS-463 steel gave evidence of having even fewer inclusions than NBS-461. For these reasons, NBS-463 steel was chosen for study. The composition of this steel is given in table 1.

To extend this work into the realm of non-ferrous materials, a decision also was made to investigate samples of recently prepared NBS brass standards. Cartridge brass samples designated 1102 (wrought) and C1102 (chill-cast) were chosen. These samples have the same analysis, but different metallurgical structures, and certification has been made for some eleven trace elements in addition to those normally specified. Both the wrought and chill-cast forms were characterized in order

Table 1. NBS spectrographic low-alloy steel standard
No. 463 provisional certified analysis
(Revised May 5, 1965.

Element	Wt (%)	Element	Wt (%)
Fe.....	(96.02) ^a	B.....	0.0012
C.....	0.19	As.....	0.10
Mn.....	1.15	W.....	0.10 ₅
P.....	0.031	Zr.....	0.20
S.....	(0.02)	Nb.....	0.19 ₅
Si.....	0.41	Ta.....	0.15
Cu.....	0.47	Al.....	0.02 ₇
Ni.....	0.39	Co.....	0.01 ₃
Cr.....	0.26	Pb.....	0.012
V.....	0.10	Ag.....	(0.0002)
Mo.....	0.12	Ge.....	(0.002 ₅)
Sn.....	0.013	O.....	(0.007)
Ti.....	0.010	N.....	(0.00 ₆)--

^a Values in parenthesis are not certified, but are given for information on the composition. Iron percent is by difference.

to observe possible differences or difficulties attendant on the use of either form.

The metallurgical procedure followed in the preparation of the standard has been described in detail elsewhere [2]. The composition of the brass is shown in table 2. The entire slab from which the brass standards were taken was checked for macro-homogeneity by several methods and found to be entirely satisfactory [2].

Table 2. NBS spectrographic cartridge brass standards
C1102 and 1102 provisional certified analysis
(revision of July 31, 1964).

Element	Wt (%)	Element	Wt (%)
Cu.....	72.8 ₅	As.....	0.004
Zn.....	27.1 ₀	Be.....	0.0000 ₃
Pb.....	0.020	Bi.....	0.000 ₅
Fe.....	0.011	Cd.....	0.004 ₅
Sn.....	0.006	Mn.....	0.004 ₅
Ni.....	0.005	P.....	0.004 ₈
Al.....	0.0007	Si.....	(0.002) ^a
Sb.....	0.005	Ag.....	0.0010
		Te.....	0.000 ₃

^a Values in parenthesis are not certified, but are given for information on the composition.

3. PROCEDURE AND RESULTS FOR BRASS

3.1 Specimen Preparation

It is a generally accepted precept that a polished unetched sample free from surface defects is the most desirable for electron probe examination. Since brass is a "soft" metal, it was feared that smearing might occur on polishing. The procedure commonly adopted is to polish, etch to remove the smeared layer and also to reveal small underlying scratches, repolish, re-etch, then repeat until the desired surface is achieved. The final surface should be free from scratches under examination at several magnifications when the sample undergoes a

full rotation while being viewed in polarized light.

As a first step, the hardness values of the wrought and cast brasses were compared with those of pure copper. The Knoop hardness number (200 g load) of the wrought material was 135 while that of the cast material was 117. Pure copper registered a Knoop value of 75. Based on these results, it was felt that the two brass forms could be polished with the same technique and that the smearing problem would be roughly comparable to that encountered with copper.

The samples were polished on water lubricated SiC papers through 600 grit. They were then finished on six micron diamond on rayon followed by 1/4-micron diamond on microcloth. The surfaces were scratch free, but a large number of what appeared to be grey inclusions were observed in the wrought and cast brasses, the number being larger in the cast form. No such inclusions were observed in pure Cu carried through the same procedure.

Under microprobe examination, these "inclusions" were found to be essentially silica in both forms of brass. They were cathodoluminescent under the beam, glowing a dull blue. Since Si is present only at a 20 ppm level in the brass, it was suspected that the "inclusions" were really artifacts due to polishing. Therefore, the samples were repolished on Al_2O_3 papers and finished on the diamond as before. Under these conditions, far fewer "inclusions" were observed. However, microprobe examination indicated some Al in the inclusions but

no Si. It was concluded that the abrasive was driving itself into the brass during rough polishing.

As a check to determine whether this disturbing phenomenon was peculiar to only the NBS standards, some ordinary commercial brass was obtained. After receiving the same preparation as the standards, similar "inclusions" were observed. Under microprobe examination Si and no Al was found after SiC papers were used while the reverse was observed after Al_2O_3 papers were used. Thus, the phenomenon does not appear to be confined to the NBS standards but appears rather more general.

In view of these results, a different sample preparation procedure was required. At first, microtomy followed by electropolishing was tried. Finally, the as-received brass was given a deep electropolish directly. The bath was 40% H_3PO_4 in water, running at 2 - 3 v and relatively low current densities. The result was a "hilly" surface suitable only for inclusion examination. Samples prepared in this fashion were used only for inclusion identification.

For structural examination and microprobe examination for matrix homogeneity, the procedure using Al_2O_3 papers was adopted since only a small amount of abrasive pick-up was noted. To minimize time on the Al_2O_3 papers, a "Norbide" (BN) abrasive wheel can be used; this may, however, pit the sample.

The structure of the wrought brass is shown in figure 1. The grains are seen to be twinned, reasonably equiaxed, and variable in size. The ASTM grain size is 0.035 to 0.045 mm

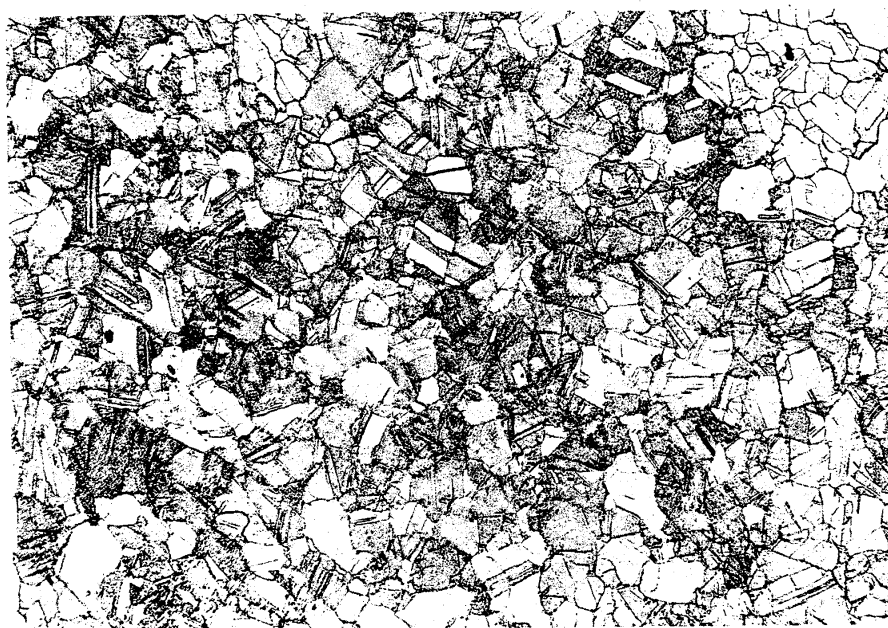


Figure 1. NBS-1102 brass (wrought) X 100.

based on comparison with the standard charts [3].

The structure of the cast brass near the chill-cast face is shown in figure 2 while the structure $3/4$ inch above the chill-cast face, i.e. at the top of the issued standard, is shown in figure 3. As expected, the dendritic cross-section at the top is larger than that at the chill-cast face. For the wrought structure, 75 to 100 grains occupy the same area as the average dendrite cross-section at the chill-cast face. For the wrought structure, 300 to 400 grains occupy the same area as the average dendrite cross-section at the top of the chill-cast standard.

The cast form exhibits a porosity which is typical of contracted gas blowholes in cast copper alloys [4].

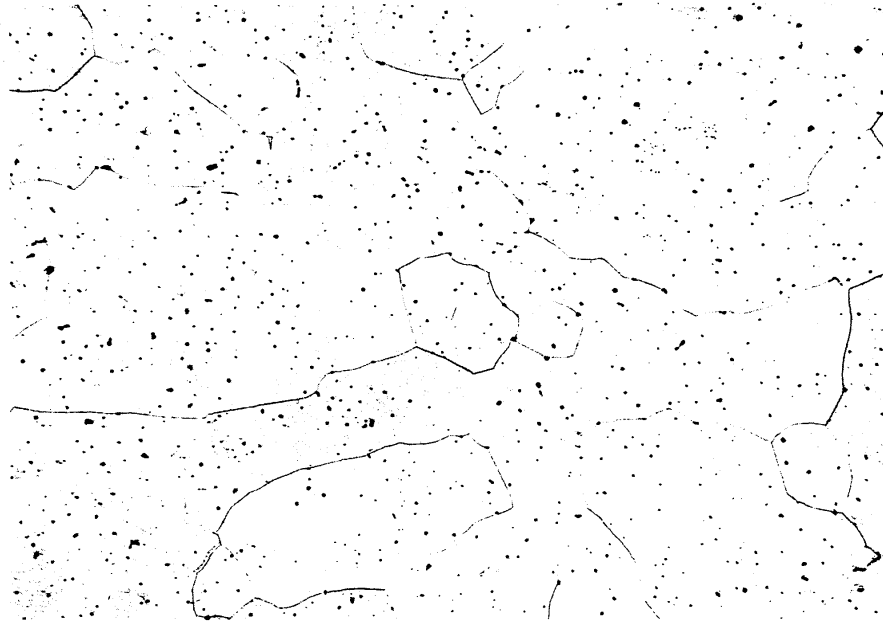


Figure 2. NBS-C1102 brass (cast) near chill-cast face X 50.

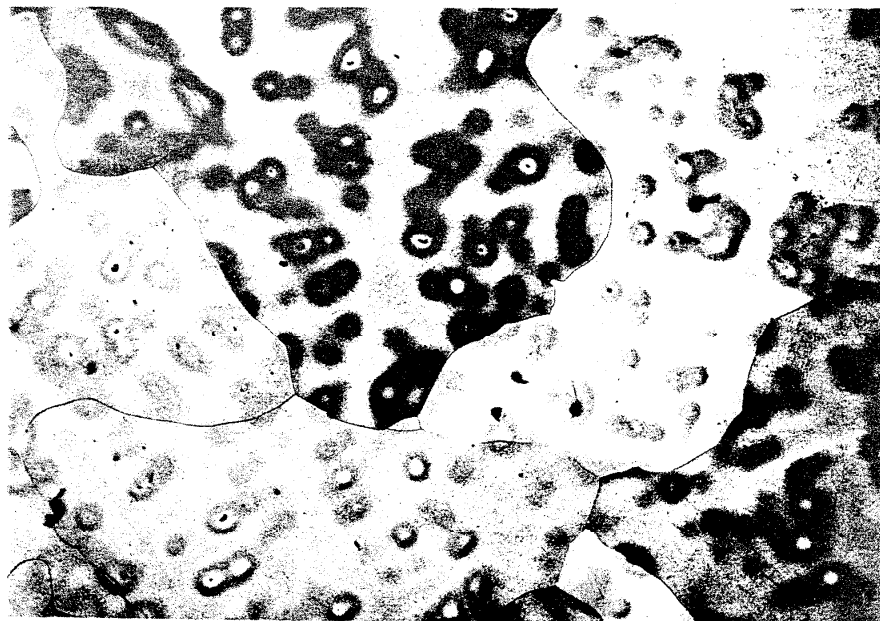


Figure 3. NBS-C1102 brass (cast, about 3/4 inch above chill-cast face X 50. Note subdendritic structure.

Figure 4 shows several small gas holes near the chill cast face. These irregularly shaped holes range in size from one to about ten microns and are located primarily at the dendrite boundaries.

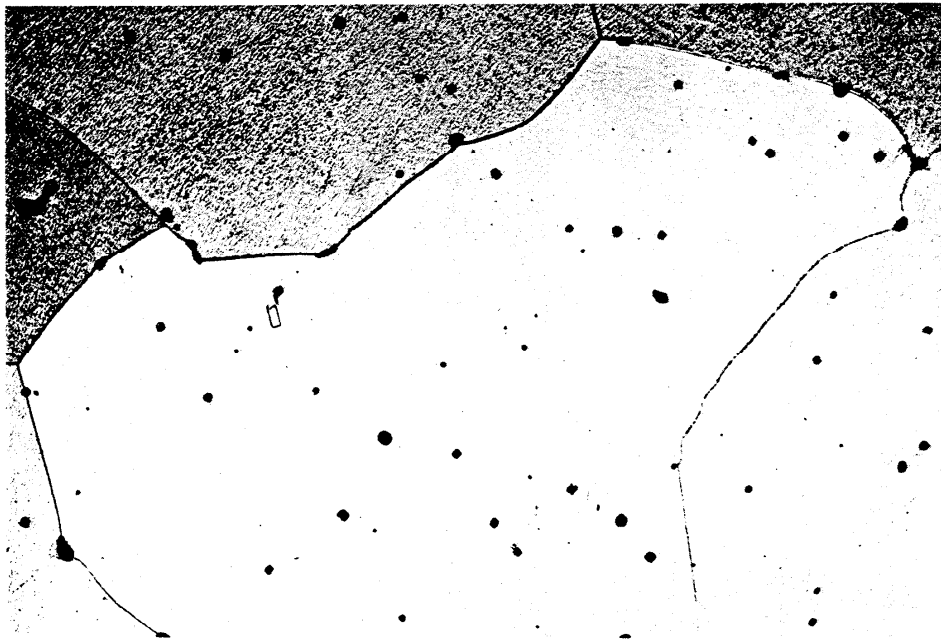


Figure 4. NBS-C1102 brass (cast), typical blowholes in cast copper-base alloys are shown X 200.

Some true inclusions were observed in both the wrought and cast forms after the sample preparation problems were overcome. These are extremely small and appear to be essentially round indicating that they are spheres in three dimensions. The size of the inclusions ranges from submicron to about two microns in diameter. They are a dull grey in color. In the cast form, they are randomly distributed and are, on the average, slightly larger at the top of the sample than near the chill-cast face.

In the wrought samples they are usually found ~~at the grain~~ boundaries; several samples cut from different samples of the standard confirmed this.

By counting inclusions in the polished and etched section, it was determined that about 200 are present lying in the entire cast face of the standard as issued, i.e., $1 \frac{1}{4} \times 1 \frac{1}{4} \times \frac{3}{4}$ inch samples. If these are assumed to be spheres of two micron diameter, there are then about 800 such inclusions per cubic millimeter of metal. The ratio of brass volume to inclusion volume is over one hundred million to one. If it is assumed that the sample for the usual microanalytical technique is a sphere 50 microns in diameter, the probability of obtaining one inclusion in such a sample is negligible. The probability for a random one micron probe to strike such an inclusion is less than one in two million.

3.2. Inclusion Identification

The true inclusions were subjected to qualitative electron probe analysis. In both the cast and wrought forms, the results essentially were identical. The inclusions are cathodoluminescent; they glow with an orange-gold color under electron excitation at 30 keV. Wavelength scans were taken of several inclusions in both forms of the brass.

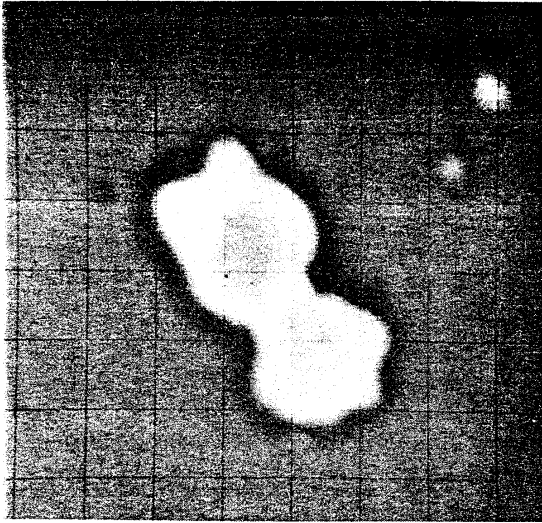
The presence of reasonably large amounts of Pb and S was noted. Some variable amounts of Zn, Si and Al were also found. The concentration of these elements varied considerably from inclusion to inclusion. No other elements were indicated to

be present. Approximately twenty such inclusions were examined in each form of the brass. A set of typical scanning display pictures (figure 5) illustrates the presence of Pb, S, Si, Al and Zn and the absence of Cu.

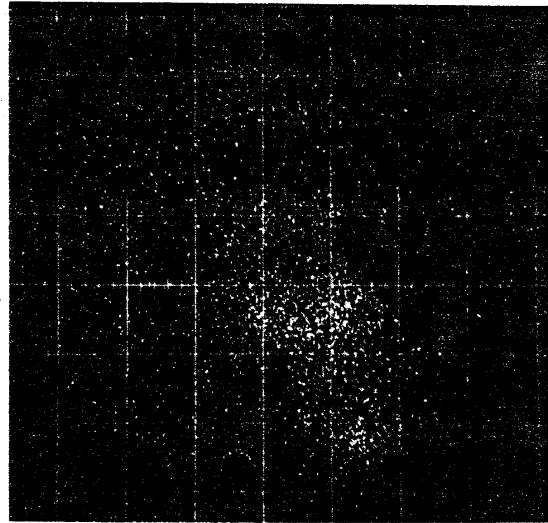
These results indicate that Pb and Si cannot be uniformly distributed within the brass. Although not appearing on the certificate of analysis, chemical determinations had been made for sulfur with an averaged result of 0.002%. The sulfur probably was introduced during the melting from the charcoal cover [2]. Figure 5 shows that the Al and Si appear to be at the same location within the inclusions. Unfortunately, the presence or absence of other impurities, such as carbon; which might have originated from the same source could not be checked with the electron probe microanalyzer available.

3.3. Homogeneity of the Matrix

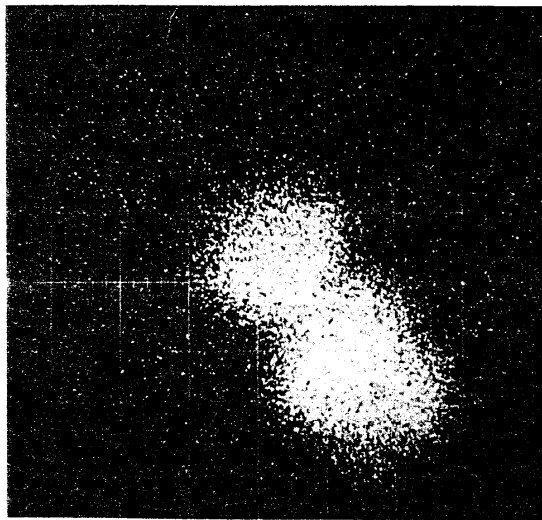
The homogeneity of the sample in Cu and Zn was investigated by means of the electron probe microanalyzer. Two separate channels using LiF analyzing crystals and sealed proportional detectors were employed. The instrument was operated at 30 keV with probe currents of 100 nanoamps. The probe diameter was approximately one micron. The count rate for Cu was on the order of 13,500 c/s whereas the count rate for Zn was on the order of 4000 c/s. Signal-to-background ratios for Zn were greater than 100 to 1.



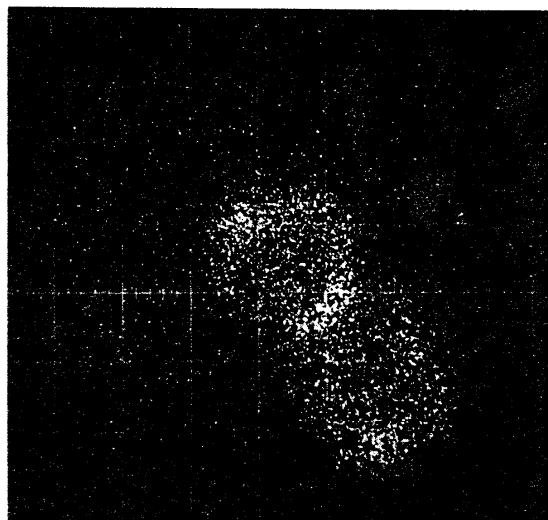
A



B



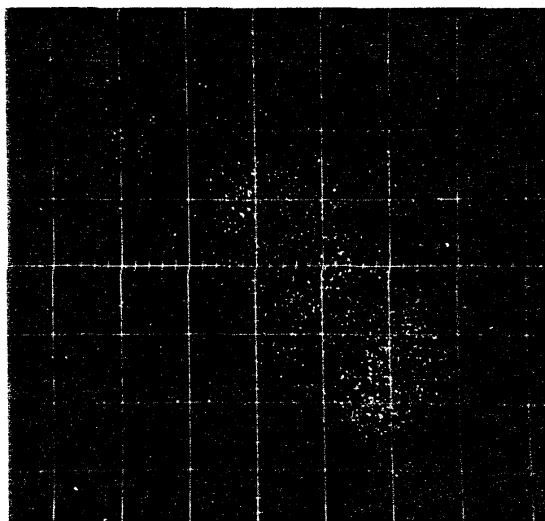
C



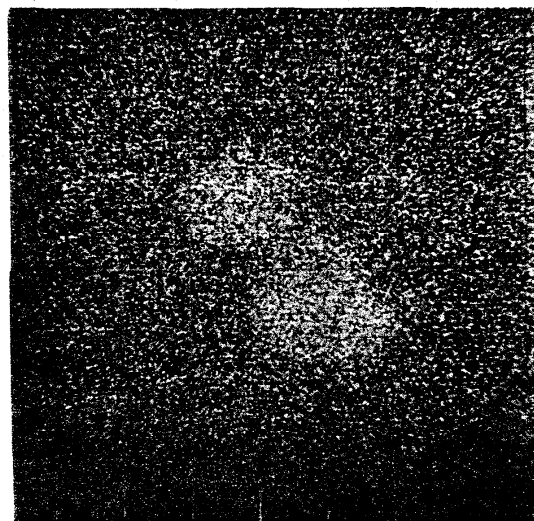
D

Figure 5. Electron beam scanning pictures of a typical brass inclusion. All X 430.

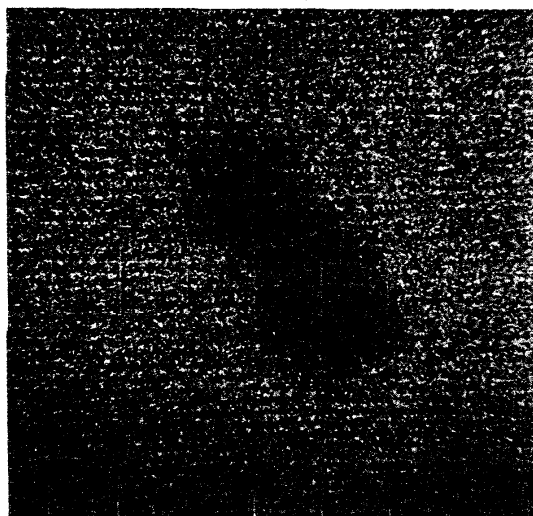
A. Specimen current. B. Pb-M_β x-ray. C. S-K_α x-ray. D. Si-K_α x-ray. E. Al-K_α x-ray. F. Zn-K_α x-ray. G. Cu-K_α x-ray.



E



F



G

Figure 5. (cont'd) Electron beam scanning pictures of a typical brass inclusion. All X 430.

A. Specimen current. B. Pb-M_β x-ray. C. S-K_α x-ray. D. Si-K_α x-ray. E. ²⁷Al-K_α x-ray. F. Zn-K_α x-ray. G. Cu-K_α x-ray.

A set of random mechanical line scans was run on each brass form as a preliminary step. These were designed to show up fairly gross inhomogenities of Cu and Zn, and also to see whether or not random striking of a blowhole or inclusion would occur. Some three scans of about five millimeters total length were run on both forms of the brass. No effect of striking an inclusion or hole was observed since there was never any drastic reduction in intensity of the Cu and Zn signals simultaneously.

The scan rate was 1.6 microns per second; hence, about 8000 counts per micron were obtained for Cu and about 2500 counts per micron were obtained for Zn. Therefore the statistical fluctuation (three standard deviations) was approximately 3% for Cu and 6% for Zn. No fluctuation greater than this was observed for either Cu or Zn in any of the line scans which represented 15,000 one micron samplings for each brass form.

Other sources of fluctuation were probe instability and non-flatness of the sample. With the former, the Cu and Zn count rates would vary in the same fashion, i.e., both would decrease gradually if the probe current decreased and vice versa. Since Cu plus Zn comprises 99.95% of the sample, no real double effect should be observable.

Sample flatness problems can be solved by properly aligning the spectrometers. If the spectrometer is properly aligned, a raising or lowering of the sample produces a decrease in count rate. Hence, a double effect similar to that for probe instability would result if the sample height with respect to the

spectrometer were changed.

After the line scans were completed, point counts in each form of the brass were taken. Twenty-four points were taken at random in the wrought sample, while forty-two points were taken in the cast sample, distributed more or less evenly along the twelve line segments of a "tic-tac'toe" grid extending across the entire specimen. Each point was counted twice for both Cu and Zn as an internal check on probe stability. The two counts were always statistically in agreement. The sample was refocused in the light optics at each point. Two separate operators took points on each sample.

The results for the cast form of the brass show that the point giving the highest Zn count rate is +1.3% higher in apparent Zn concentration than the mean. The results for the lowest Zn point give a value 2.2% below the mean. The standard deviation for counting error is 0.37% (mean total number of Zn counts accumulated, N, was 79,224). The standard deviation computed from the 42 determinations of Zn content is 0.79%.

If the mean Zn count is considered to correspond to the certified value of 27.10%, the analytical range corresponding to two standard deviation limits is 26.7% to 27.5%. The average sampling was about 10 cubic microns of the brass per point; this corresponds to about 10^{-11} g of brass. Results for both brass forms are given using the foregoing notation in table 3.

Table 3. Analytical results for Cu and Zn in NBS-C1102 and 1102 cartridge brass.

Element	Coefficient of variation for counting	Standard deviation (%) computed from experiment	Analytical range (two standard deviation limits) of composition at three micron level of spatial resolution
Zn ^a	.0036	0.79	26.7 to 27.5
Cu ^a	.0027	0.72	71.8 to 73.8
Zn ^b	.0036	2.2	25.9 to 28.3
Cu ^b	.0019	1.0	71.1 to 74.6

^aCast
^bWrought

3.4. Electron Probe Microanalysis Results

As the final proof; it was deemed necessary to perform a complete electron probe microanalysis of each brass standard for both Cu and Zn. This was done as a separate experiment approximately ten days after all other data had been taken.

The voltage used was 30 kV while a constant incident beam current of 50 nanoamps was employed. This resulted in a count rate of about 10,000 c/s in pure Cu and 5500 c/s in pure Zn using LiF crystals in conjunction with sealed proportional counters. Some five points each of Cu and Zn were recorded on both brasses. Background was counted ± 0.05 Å off peak for Cu and ± 0.1 Å off peak for Zn. It is interesting to note that the background count for both Cu and Zn was about the same in

the pure element as in the brass. The x-ray emergence angle was 52.5° .

The lines examined were Zn- K_{α} and Cu- K_{α} . The Duncumb corrected Philibert equation [5] was used for absorption correction in Zn; the correction required was found to be less than 0.1%. The Castaing fluorescence correction for Cu- K_{α} being fluoresced by Zn- K_{β} was used [6]. Mass absorption coefficients for both K_{α} and K_{β} lines were taken from Heinrich [7]. The results are shown in table 4.

Table 4. Electron probe microanalysis results for NBS-C1102 and 1102 brasses.

<u>Element</u>	<u>Form</u>	<u>Apparent (%)</u>	<u>Actual (%)</u>
Cu	Cast	73.4	72.5
Zn	Cast	27.8	27.8
Cu	Wrought	73.4	72.5
Zn	Wrought	27.7	27.7

As can be seen, the results in table 4 agree very well with the certified values of 72.85 for Cu and 27.10 for Zn. As predicted, the agreement between the cast and wrought forms is excellent. These results have been corroborated by 5 other electron probe laboratories who received wrought and cast pieces cut at random from different samples of the brass.

It is suggested that because of the very small difference between apparent and true concentrations these brasses can be

used to calibrate electron probe microanalyzers. Thus, an operator could check to see that the instrument is giving proper relative intensity data at various times during an experiment by merely taking five minutes to check the Cu and Zn values in the brass.

3.5. Summary and Conclusions for Brass

The cast form of the cartridge brass designated NBS-C1102 shows no evidence of inhomogeneity greater than about 1.6% of the amount present for either Cu or Zn for samples of 10⁻¹¹ g.

Therefore, this is the maximum degree of inhomogeneity to be expected for any technique sampling a larger amount of the brass.

The wrought form shows an apparently larger degree of inhomogeneity which is 2.0% for Cu and 4.4% for Zn. Nevertheless, neither of these figures is prohibitive when micron sized analytical samples are to be investigated.

Both forms contain small inclusions which are comprised of variable amounts of lead, sulfur, aluminum, zinc, and silicon but no copper. These inclusions are easily avoided in the electron probe microanalyzer; the probability to strike an inclusion lying beneath the polished surface is negligible for any take-off angle. Likewise, the probability for the inclusions to affect any analysis by one percent is negligible for those elements not present in the inclusions.

Care must be taken in the surface preparation of the brass to avoid occlusion of materials. Care also should be taken

to make sure that an undisturbed structure is being analyzed. It is asserted that when these precautions are taken that NBS cartridge brass 1102 or C1102 can be used for any present day microanalytical technique with little chance of inaccuracy due to inhomogeneity. Electron probe microanalysis results confirm this assertion.

4. PROCEDURE AND RESULTS FOR STEEL

Steel samples were metallographically polished until no scratches were observed when the specimen was viewed in polarized light. The as polished surface is shown in figure 6; the inclusions are readily apparent. The etched structure in figure 7 shows a large number of small spheroidized carbides. The average carbide diameter appears to be one to two microns.

Figure 6. NBS-463 steel, as polished X 200.

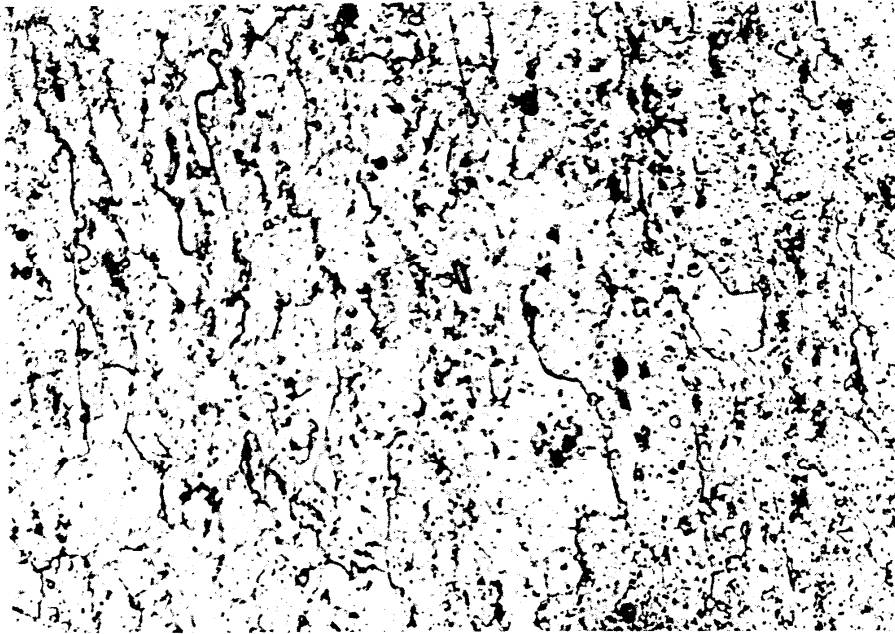


Figure 7. NBS-463 steel, etched structure in longitudinal section X 1000.

4.1. Inclusion Identification

Since all constituents except iron are present at low levels, it was felt that a concentration of any element within the inclusions would preclude the possibility of that element being homogeneous within the steel. Therefore, the inclusions were investigated first.

Surprisingly, three distinct types of inclusions were observed. These are shown marked in figure 8. The first is a plain straight edged small inclusion which is yellow and which is fairly plentiful. Such inclusions were found to contain a large proportion of Zr and some Cr. Scanning electron probe pictures illustrate this (figure 9). No other elements of atomic number greater than 11 could be found.

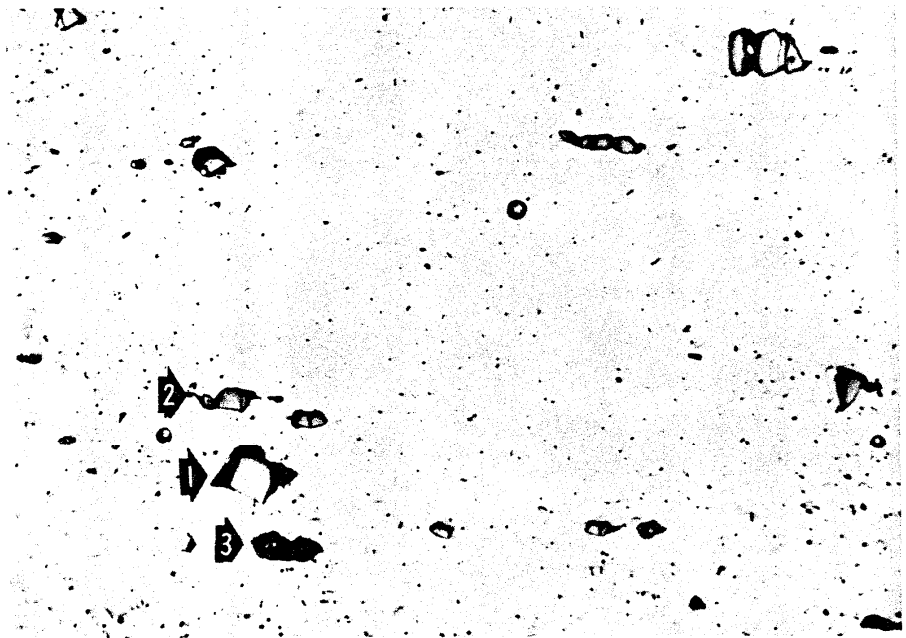
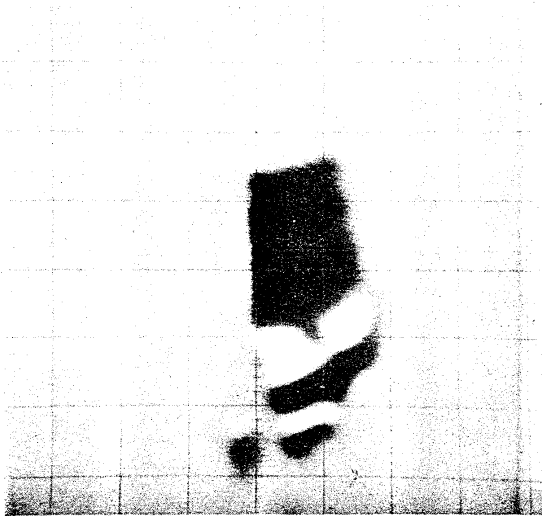


Figure 8. NBS-463 steel, three distinct types of inclusions X 1000.

The second type of inclusion resembles a stringer. It is a composite and is grey. These contain Zr, Ta, Nb and a trace of S. No other detectable elements were found. Scanning pictures are shown in figure 10 except for S which gave too weak a signal for photography.

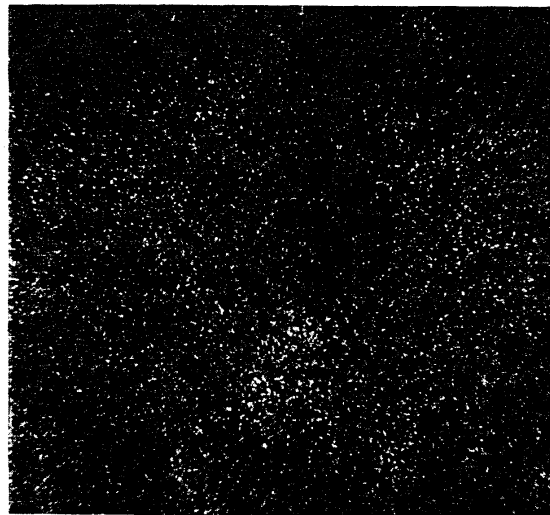
The third type of inclusion is not plentiful. It is a small greyish composite which is cathodoluminescent, glowing a light beryl blue under the electron beam. These inclusions contain only Zr and S among the detectable elements. It is surmised that they consist largely of ZrO_2 . The scanning photographs are shown in figure 11. It should be mentioned that iron is depleted in all three types of inclusions.



A



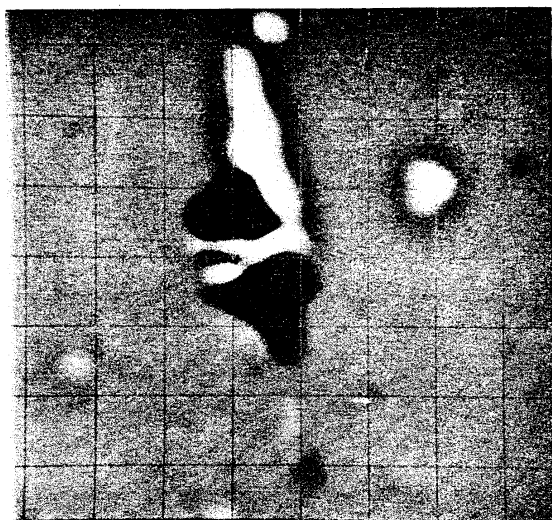
B



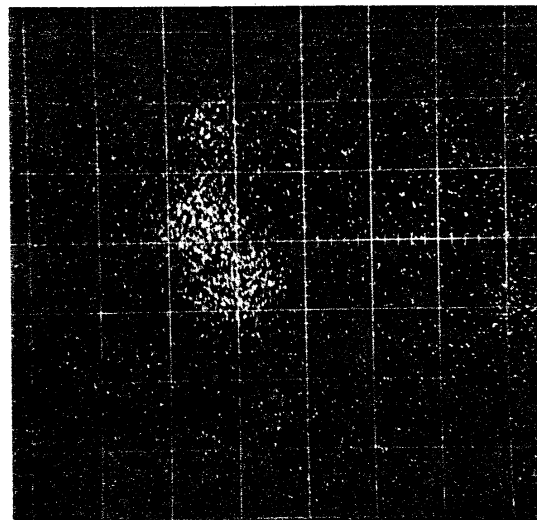
C

Figure 9. Electron beam scanning pictures of steel, inclusion 1. All X 430.

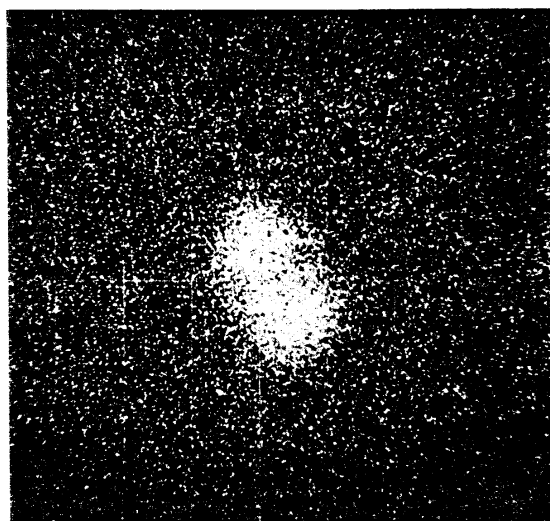
A. Specimen current. B. Zr-L_α x-ray.
C. Cr-K_α x-ray.



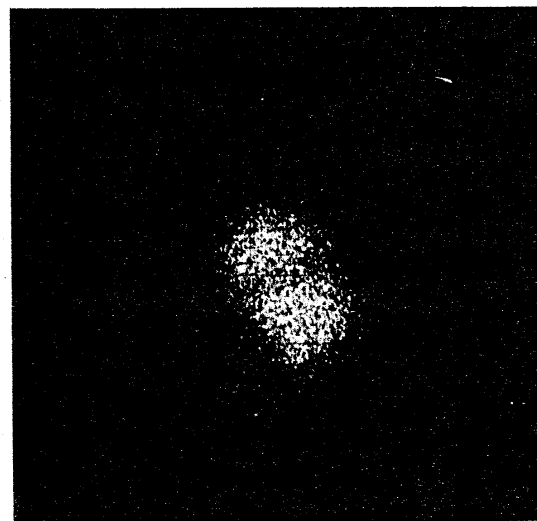
A



B



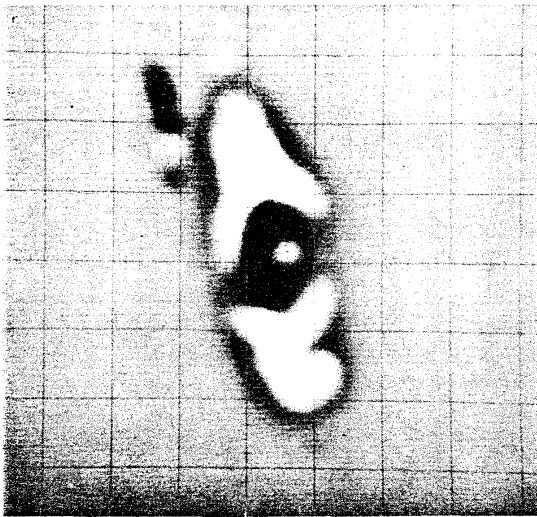
C



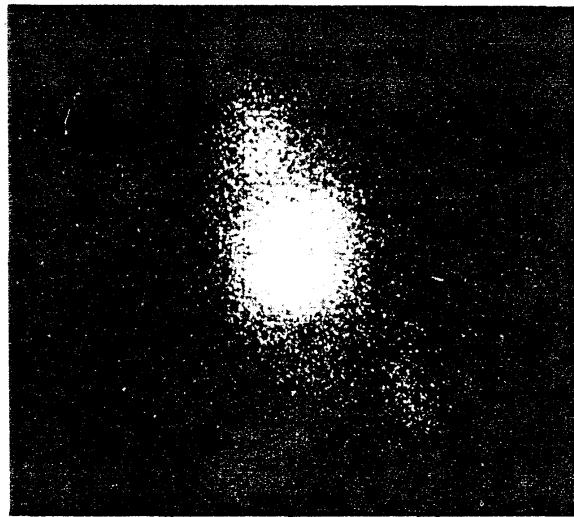
D

Figure 10. Electron beam scanning pictures of steel, inclusion 2. All X 430.

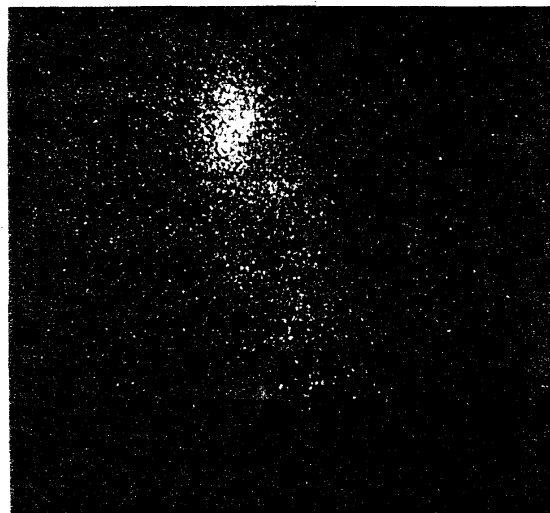
A. Specimen current. B. Zr- L_{α} x-ray.
C. Ta- L_{α} x-ray. D. Nb- L_{α} x-ray.



A



B



C

Figure 11. Electron beam scanning pictures of steel, inclusion 3. All X 430.

A. Specimen current. B. Zr-L_α x-ray.
C. S-K_α x-ray.

4.2. Tests for Other Elements

A mechanical line scan of Mn concentration was run at a rate of 1.6 microns per second. The line-to-background ratio was 6 to 1. A portion of the recording of this scan is shown in figure 12. The Mn concentration is seen to fluctuate as much as twenty percent about the mean over relatively short distances. Area scans confirmed the observation that Mn is not uniformly distributed.

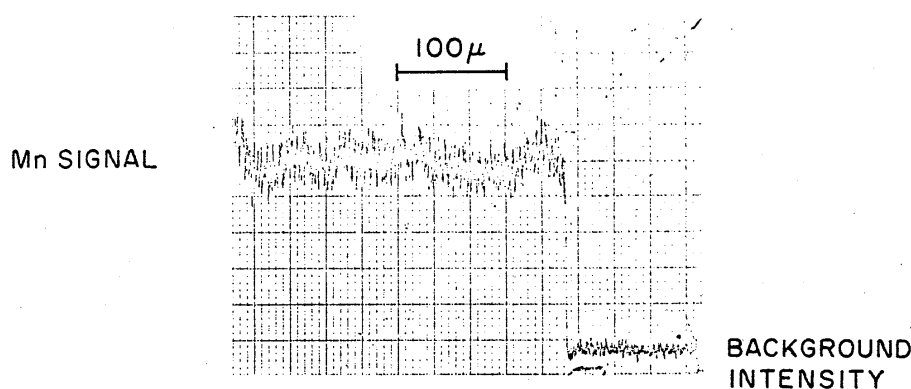


Figure 12. Portion of line scan for Mn in NBS-463 steel.

Point counts away from inclusions were made for Fe, Cu, Ni, and Si. Two different operators alternated in taking the data. Each point was randomly picked and counted twice in the same fashion as the brass; the sample was refocused in the light optics at each point. The results for each of these elements are presented in table 5.

4.3. Summary and Conclusions for Steel

Of the ten elements in the steel investigated, five were found to be concentrated in one or more of three distinct types

Table 5. Analytical results for Fe, Cu, Ni, and Si in NBS-463 steel.

Element	Coefficient of variation for counting	Standard deviation (%) computed from experiment	Analytical range (two standard deviation limits of composition at three micron level of spatial resolution)
Fe ^a	.0032	1.6	92.9 to 99.2
Cu ^b	.0154	4.4	0.43 to 0.51
Ni ^b	.0195	6.0	0.35 to 0.43
Si ^c	.0078	2.9	0.39 to 3.43

^aThirty two points examined.

^bThirty four points examined.

^cTwenty five points examined.

of inclusions. These were Ta, Nb, S, Cr and Zr. It is therefore concluded that the steel is unsuitable as a micro-analytical standard for these elements.

Additionally, manganese was found to be non-uniformly distributed. This element is not concentrated in inclusions. However, four elements namely Fe, Cu, Ni and Si were found to exhibit uniform distribution within the matrix of the steel. Each is depleted within the inclusions.

Assuming roughly the same number of inclusions in NBS-463 steel as was determined present in NBS-461 steel, (the actual number in NBS-463 is less) approximately the same probabilities concerning the inclusions should apply [1]. Thus, the probability for a random one micron probe to strike an inclusion is about 1 in 350 and about one inclusion should

occur per fifty micron sphere of steel sample. For a sampling procedure, which scans a large area of the surface, a number of elements may show compositional fluctuations from one test to another.

It is concluded that Cu, Ni and Si in NBS-463 steel can be analyzed by any microanalytical technique with little chance of error due to inhomogeneity. Iron is a borderline case if one is seeking absolute accuracy. The elements Ta, Nb, S, Cr, Zr, and Mn should not be used in the steel for microanalytical standardization.

5. REFERENCES

- [1] R. E. Michaelis, H. Yakowitz, and G. A. Moore, Metallographic Characterization of an NBS Spectrometric Low-Alloy Steel Standard, J. Res. NBS 68A, 343 (1964). Issued in expanded form as NBS Misc. Publ. 260-3, 1-17 (1964).
- [2] R. E. Michaelis, L. L. Wyman, and R. Flitsch, Standard Reference Materials: Preparation of NBS Copper-Base Spectrochemical Standards, NBS Misc. Publ. 260-2, 1-36 (1964).
- [3] 1964 Book of ASTM Standards, "Standard Methods for Estimating the Average Grain Size of Metals" Part 31, 225 (Plate III) (1964).
- [4] E. P. Polushkin, Defects and Failures of Metals, Elsevier Publishing Company, New York, p. 47 ff, 1956.
- [5] P. Duncumb and P. K. Shields, Effect of Critical Excitation Potential on the Absorption Correction in X-ray Microanalysis, Tube Investments Research Laboratories Technical Report No. 181, 1-9 (1964).
- [6] R. Castaing, Application of Electron Probes to Local Chemical and Crystallographic Analysis, Thesis to University of Paris, p. 83 ff, 1951.
- [7] K. F. J. Heinrich, X-ray Absorption Uncertainty, Proc. Symp. Elect. Probe Microanal. Wash. D. C. 1964, J. Wiley and Sons, Publishers. In press.